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Biochar – synergies between carbon storage, environmental functions and renewable energy production

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Declaration

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The thesis contains four chapters in press or intended for publication in peer-reviewed journals. The details of each proposed publication and contribution of the candidate and co-authors' work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others. Furthermore the thesis has not been submitted in any previous application for a degree.

The candidate, as lead author, was solely responsible for all experimentation, laboratory analysis (unless stated otherwise), data analysis and writing of the papers. Co-authors provided guidance and support on the scope and design of the project, the analyses performed and contributed to the editing of the manuscript.

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Lay Summary

Since the start of the industrial revolution the burning of fossil fuels has caused the atmospheric concentration of greenhouse gases (GHG) to rise with carbon dioxide (CO_2) being recognised as the largest contributor to total GHG emissions (76 % in 2010). The atmospheric level of CO_2 is quickly approaching a dangerous level and so limiting the release of CO_2 coupled with long term storage is essential to prevent the most damaging effects of climate change. The combustion of biomass, rather than fossil fuels, can contribute to global energy demands, however this process lacks a storage option and so is only considered to be carbon neutral. Therefore, through a process called 'pyrolysis', biomass is heated rather than burned resulting in the production of carbon negative biofuels as well as a solid product known as 'biochar'.

Biochar is a material, largely consisting of carbon (C), which once placed in soil can lead to improved soil fertility, reduced GHG emissions and, most importantly, long term storage of C. However biochar research is in its infancy which means many questions still remain unanswered: What effects do biochar production conditions have on its performance in soil? How stable is biochar in soil? How does increasing one benefit of biochar, such as C storage, impact other biochar benefits e.g. soil enhancement and heat/power generation? To attempt to answer these questions biochar samples (> 80 experiments) were produced under different pyrolysis conditions (temperature, rate of heating, feedstock type etc.) and analysed for important chemical and functional properties. The main findings of this study demonstrated that pyrolysis at higher temperatures resulted in: (1) Increased C stability and overall C storage potential. (2) Improved functional properties which could improve the soil enhancing ability of biochar. However increasing the pyrolysis temperature did not favour all functional properties. This therefore demonstrated the need for further consideration over which final properties of biochar were of more importance. (3) A higher potential energy output of the pyrolysis system without sacrificing the long term C storage ability of biochar. (4) The production of a single biochar product which demonstrated favourable properties that could benefit C storage, soil enhancement and biofuel production.

Abstract

Growing concerns about climate change and the inevitable depletion of fossil fuel resources have led to an increased focus on renewable energy technologies and reducing GHG emissions. Limiting the atmospheric level of CO_2 is essential to prevent the most damaging effects of climate change. Among renewable energy resources, biomass combustion has the largest potential to contribute to global energy demands, however it is considered to be a carbon neutral solution and so only limits CO_2 concentrations rather than reducing them. Through pyrolysis rather than combustion, biomass can lead to carbon negative liquid, gaseous and solid fuels while also offering a route for long term carbon storage in the form of biochar. Biochar is a carbonaceous material which has shown potential for improving soil fertility, reducing GHG emissions and most importantly long term C storage in the environment. However many questions still remain unanswered with regard to biochar, especially the influence that process conditions can have on its performance in soil as well as any potential trade-offs between soil amendment, C sequestration and heat/power generation. This thesis is therefore focused on assessing the influence that process conditions and feedstock selection have on biochar properties related to carbon stabilisation, improving soil fertility (functional properties) as well as the distribution of energy amongst the pyrolysis co-products. To achieve this, a systematic set of biochar samples was produced, using a wide range of pyrolysis parameters (highest treatment temperature (HTT), heating rate, residence time, carrier gas flow rate and feedstock type), and analysed for physicochemical and functional properties. Pyrolysis HTT consistently showed a dominant influence on determining the final yields and properties of biochar, while the effect of other production parameters was varied.

In this thesis the candidate first studied the effect that process conditions had on the long term stability of biochar, as an important indicator of its ability to sequester carbon. While increasing the HTT resulted in a decrease in biochar yield, overall the yield of stable-C increased with temperature. This meant that by applying a higher HTT during pyrolysis a higher C sequestration potential for biochar was achieved. Next to be examined was the influence that process conditions had on other

functional properties (labile-C yield, biochar pH, extractable nutrients and cation exchange capacity (CEC)) was then examined. The labile-C yield of biochar decreased with increasing HTT due to the release of volatile matter, while the CEC and concentration of extractable nutrients tended to be higher in biochar produced at 450^{o}C rather than greater HTTs. Biochar pH was also highly alkaline at elevated HTT. This indicated that while high HTT favoured C sequestration and biochar pH, lower HTT may be more favourable for other functional properties. Furthermore by assessing the mass and energy distribution amongst the solid, liquid and gaseous fractions, it was possible to determine the energy balance of the process and through this evaluate the trade-off between the C sequestration potential of biochar and the energy output of the liquid and gas fractions. As the severity of pyrolysis was raised, the total energy stored within the liquid and gaseous co-products increased at the expense of the energy content of biochar, therefore increasing the available energy output of the system and reducing the energy lost when using biochar for carbon storage rather than for bioenergy. This also demonstrated that the pyrolysis process could be fine-tuned to increase the amount of stored C while also improving the heat/power generation of the system. The higher energy content of the gas stream at elevated HTT was also seen to contain sufficient energy to sustain the pyrolysis process, which would free up the solid and liquid fractions for higher value applications while reducing the necessity for external fuel sources. Finally, the data set was used to produce statistical models enabling the prediction of biochar stable-C yield as well as the heating value of biochar.

The results of this thesis therefore demonstrate that through applying high HTT the potential energy output of the pyrolysis system can be increased while producing a biochar product with high C sequestration potential and positive functional properties for soil amendment. Due to potential trade-offs, the final choice of process conditions and feedstock would then be made based on the specific requirements of a selected site for biochar application. Understanding the influence that production conditions have on the functional properties of biochar as well as the energy balance of the system is critical to developing specifically engineered bespoke biochar, be it for agricultural use, carbon storage, energy generation or combinations of the three.

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List of Abbreviations

The following are a list of the abbreviations used throughout this thesis

AEC	Anion Exchange Capacity
ANOVA	Analysis of variance
CCS	Carbon Capture and Storage
CEC	Cation exchange capacity
CGE	Cold Gas Efficiency
CP	Conventional Pyrolysis
daf	Dry ash free basis
db	Dry weight basis
EF	Modelling Efficiency
GHG	Greenhouse-gas
HHV	Higher heating value
HTT	Highest treatment temperature
IBI	International Biochar Initiative
ICP-OES	Inductively coupled plasma – optical emission spectrometry
IPCC	International Panel on Climate Change
LCA	Life Cycle Analysis
LHV	Lower heating value
MRT	Mean residence time
MW	Microwave Pyrolysis
NPP	Net Primary Production
SOC	Soil Organic Carbon
SOM	Soil Organic Matter

TGA	Thermogravimetric analysis
UKBRC	UK Biochar Research Centre

Units

g C	grams of carbon
Gt C $year^{-1}$	Gigatonnes of carbon per year
K min^{-1}	Kelvin per minute
kj g^{-1}	kilojoules per gram
MJ kg^{-1}	Megajoules per kilogram
MJ t^{-1}	Megajoules per tonne

Feedstock

PC	Pine Wood Chips
RH	Rice Husk
SP	Straw Pellets
WC	Willow Wood Chips
WP	Softwood Pellets
WS	Wheat Straw
WSP	Wheat Straw Pellets

Chapter 1. **Introduction**

1.1 **Background**

Global climate change and the inevitable depletion of fossil fuel reserves are two major challenges facing the 21st century which have led to a research boom into new concepts and technologies for alternative energy sources and reducing GHG emissions. However humanity already possesses the scientific and industrial knowledge to solve the problem of rising atmospheric carbon dioxide (CO_2) levels over the next few decades by simply scaling up the strategies currently in place (Pacala & Socolow, 2004). At 76 % of total GHG emissions in 2010, CO_2 remains the major anthropogenic GHG with the cumulative fossil CO_2 emissions more than trebling from 420 $GtCO_2$ in 1970 to 1300 $GtCO_2$ in 2010 (IPCC, 2014). Since 2000, emissions of anthropogenic CO_2 have risen by more than 3 % per year with the net addition likely to rise to 8 – 12 GtC $year^{-1}$ by 2020 and as much as 6 – 23 GtC $year^{-1}$ by 2050 (IPCC, 2005; IEA, 2007; Mathews, 2008; Woolf *et al.*, 2010). Limiting the atmospheric level of CO_2 is essential to preventing the most damaging effects of climate change with 500 $\pm$ 50 ppm or less than 560 ppm (double preindustrial concentration) being identified as an achievable target. For a stabilisation target of 500 ppm to be realised then emissions need to be held at the 2004 level of 7 GtC $year^{-1}$ for the next 50 years (Pacala & Socolow, 2004). Pacala & Socolow (2004) imagined this 50 year emissions reduction as a perfect triangle which can be divided into several equal "wedges" as shown in Figure 1-1. Each wedge is representative of a strategy that would reduce emissions in the atmosphere by 1 GtC $year^{-1}$ by 2054. Wedges could be achieved from energy efficiency improvements (vehicle quantity and efficiency, building insolation etc.), decarbonisation of electricity and fuel supplies through low-GHG emission technologies (i.e. carbon capture and storage (CCS), nuclear power, renewable energy etc.) and biological storage in forests and agricultural soils (reduced deforestation, reforestation etc.) (Pacala & Socolow, 2004; Matovic, 2011; IPCC, 2014).

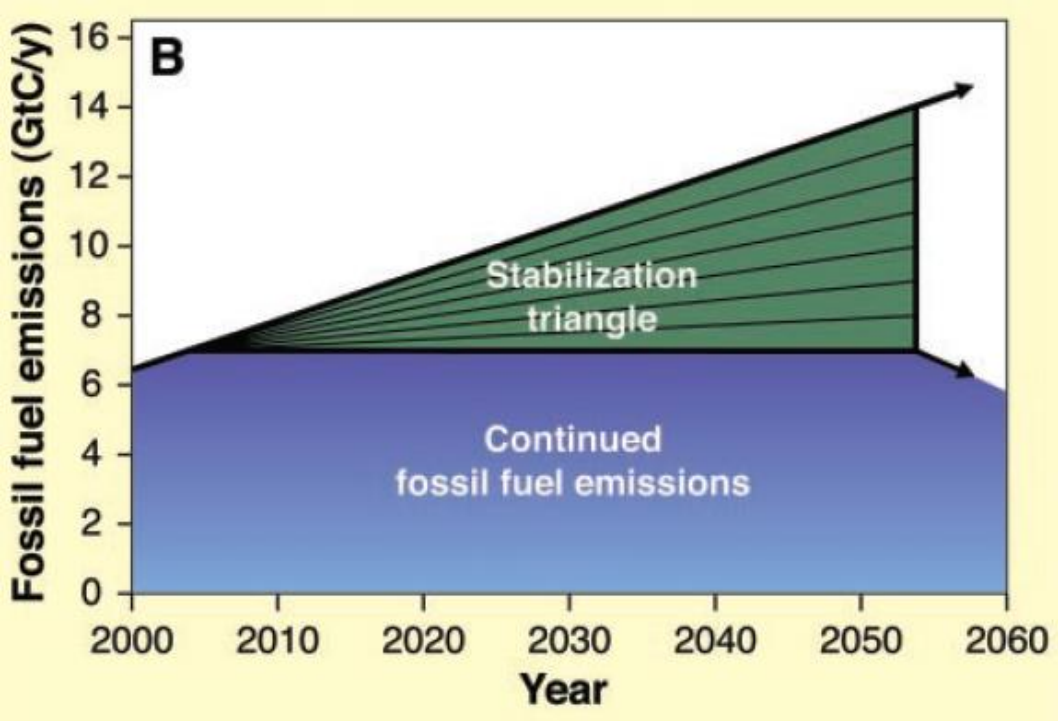

Figure 1-1: A stabilization triangle of avoided emissions (green) and allowed emissions (blue). The allowed emissions are fixed at 7 GtC year^{-1} beginning in 2004. The stabilization triangle is divided into seven wedges, each of which reaches 1 GtC year^{-1} in 2054. (Pacala & Socolow, 2004).

Biomass removes CO_2 from the atmosphere through photosynthesis and is then burned through various technologies to produce energy. With the total global production of biomass estimated at >147 billion metric tons per year it can be regarded as the single-largest renewable energy source currently being used as well as having the largest potential to contribute to global energy demands, with 10 % of the annual global primary energy supply in 2008 being attributed to biomass (Balat & Ayar, 2005; Bridgwater, 2006; Mohan *et al.*, 2006; Demirbas, 2007; Zoulalian, 2010; IPCC, 2011). Biomass combustion is widely thought of to be carbon neutral, in that the same amount of carbon absorbed through the growing of plants is released through burning. However a continuous debate between researchers focuses on the true extent on this carbon neutral footprint achieved by bio-fuels, as in practice the process can be somewhat carbon positive due to the involvement of fossil fuels during pre/post treatments such as fertiliser use, harvesting and material

transportation (Mathews, 2008). For any bio-fuel to be regarded as "carbon negative" a portion of the carbon stored in biomass must be returned to the soil or otherwise stored in a stable form. Furthermore, any strategy for removal of CO_2 from the atmosphere must have the longevity to keep CO_2 stored safely in large concentrations over a long time scale such as centuries or millennia, as the re-return of carbon into the atmosphere on too short a timescale could intensify climate change rather than alleviate it (Woolf, 2008).

The direct incorporation of crop residues to soils has been traditionally performed to maintain soil C stocks. However, these C sources have relatively short residence times in soil due to rapid mineralization over a period of 30 years or less (Lehmann *et al.*, 2006) which can also lead to increased release of methane. On the other hand, biochar C could be stabilized in soil for long periods of time. Biochar is a growing concept which could be utilised to help combat global climate change and equate to one wedge in the carbon and climate stabilisation triangle through: Direct sequestration of biochar in stable soil carbon pools; Increase in global Net Primary Production (NPP) from increased soil fertility; Displacement of carbon-positive fossil fuel energy; Reduction of nitrous oxide emissions (IBI, 2008).The International Biochar Initiative (IBI) modelled four scenarios (Conservative, Moderate, Optimistic and Optimistic plus) for biochar production. It determined that even under a conservative approach the carbon stored within biochar alone can account for up to 0.25 Gt (1/4 a wedge) by 2030, while the optimistic scenario would actually achieve 1 GtC by 2040 (IBI, 2008). By including the added benefits of reduced Fossil-C emissions associated with biochar, three of the four scenarios predicted more than 1 wedge of impact on atmospheric CO_2 levels by 2025, substantially ahead of the 2054 target. However, to fulfil its potential, extensive research is needed to answer some of the biggest questions surrounding the field.

1.2 What is biochar?

Biochar is a porous carbonaceous material produced by the thermo-chemical decomposition of organic materials in an oxygen depleted atmosphere (Demirbas &

Arin, 2002). Through this treatment approximately 50 % of the carbon contained in the original biomass can be retained within biochar (Laird, 2008; Atkinson *et al.*, 2010; Shackley & Sohi, 2010). The motivation and objectives of biochar production can be divided into four complementary areas: climate change mitigation; energy production; soil improvement and waste management (Lehmann & Joseph, 2009). The concept of applying biochar to soil for environmental benefits was first developed based on observations made on Amazonian fertile black anthropogenic soils or "Terra Preta de Indio"(Glaser *et al.*, 2001; Lehmann *et al.*, 2003). There has been little research into the long term performance and stability of biochar in soil, but studies on terra preta soils propose a mean residence time (MRT) of char in soil to be in the range of millennia, compared to the MRT of bulk soil organic matter (SOM) of 50 years. This sustained resistance to chemical and biological breakdown makes biochar a plausible solution to slowing and eventually reversing global warming (Lehmann *et al.*, 2009; Verheijen *et al.*, 2009; Sohi *et al.*, 2010; Spokas, 2010). Although having high levels of resistance, biochar is still gradually mineralized to CO_2; otherwise, SOM would be dominated by biochar accumulated over long time scales (Masiello, 2004; Cheng *et al.*, 2006). Different fractions of biochar will decompose at different rates under different conditions determined by the method of production, starting material, climate and soil properties. Terra Preta soils were also found to contain a higher SOM concentration compared to the surrounding soils (Glaser *et al.*, 2001). This observation was described by Janzen (2006) as a 'paradox' since stocks of SOM should be conserved to sequester C; however at the same time the driving force for increasing overall soil quality is the decomposition of SOM. This led to the suggestion that biochar application to soils outside of the Amazon basin would have the same potential to improve soil fertility and sequester C; however as of yet there is no clear evidence that biochar application to soil can lead to 'terra preta' like fertility (Jeffery *et al.*, 2013). The physicochemical properties of biochar could make it suitable as an option for safe and long-term storage of carbon in the environment and potential enhancement of soil (Lehmann, 2007; Laird, 2008; Woolf, 2008; Lehmann *et al.*, 2009; Verheijen *et al.*, 2009; Shackley & Sohi, 2010; IBI, 2013). Mechanisms for this positive effect could include nutrient retention,

water holding capacity, CEC, surface area etc. and these properties have been found to be greater in biochar compared to other forms of SOM, thus potentially resulting in increased soil fertility, reduced environmental pollution and carbon sequestration (Lehmann, 2007; Jeffery *et al.*, 2011). The timescale over which these benefits operate could vary greatly depending on the type of biochar. Benefits such as available nutrients and liming effect could be short lived but rapidly acting; while other properties such as CEC is slower to develop but longer lived (Jeffery *et al.*, 2013). The incorporation of biochar in soil can be seen as a 'closed-loop' system whereby biomass from agriculture or other waste is pyrolysed to biochar (with bioenergy co-products) which is then returned to the soil aiding in the growth of more biomass, creating carbon offsets for the user (Zimmerman, 2010; Jeffery *et al.*, 2013).

1.3 Biochar production

There are many important aspects to consider regarding the manufacturing of biochar, including type of production process, starting feedstock as well as the desired yield and composition of the final co-products. The following section identifies the main parameters which need to be considered and how they may influence the production of biochar.

1.3.1 Pyrolysis

Biochar can be produced by several processes of thermo-chemical conversion such as pyrolysis, gasification, hydrothermal carbonisation etc. (Balat *et al.*, 2009; Meyer *et al.*, 2011; Bridgwater, 2012; Manyà, 2012). Pyrolysis, from the Greek word 'pyro' meaning fire and 'lysis' meaning decomposition, is the decomposition of organic material at elevated temperatures in the complete or partial absence of oxygen. The definition of pyrolysis has changed over time with old literature referring to pyrolysis as the carbonization of biomass to produce a primary solid char product, while in today's literature the term can often describe a process where any one of liquid, gas or char products are preferred (Mohan *et al.*, 2006). However the fundamental

mechanisms of pyrolysis remain the same and can be simplified into several main steps (Demirbas, 2004; Mohan *et al.*, 2006):

1) Transfer of heat from a heat source, to increase the temperature inside the fuel resulting in release of moisture;

2) As temperature rises the start of primary pyrolysis reactions leads to release of volatiles and formation of char;

3) Heat transfer between hot volatiles and cooler unpyrolyzed fuel is caused by the flow of hot volatiles towards cooler solids;

4) Condensation of volatiles in the cooler regions of the fuel, followed by secondary reactions, can lead to tar production;

5) Autocatalytic secondary pyrolysis reactions occur simultaneously in competition with primary pyrolytic reactions;

6) Depending on the process's residence time/temperature/pressure profile, further thermal decomposition, reforming, water gas shift reactions, radical recombination and dehydration can occur.

This process causes biomass to undergo reactions such as dehydrogenation, demethylation and decarboxylation leading to the formation of pyrolysis gas, liquid products and a solid carbon rich residue known as biochar (Demirbas & Arin, 2002; Lehmann & Joseph, 2009; Verheijen *et al.*, 2009; Novak & Busscher, 2013). The type of pyrolysis used for biomass conversion can have a substantial effect on the final properties and application of the solid, liquid and gaseous co-products.

1.3.2 **Technologies**

Pyrolysis has long been established as a viable technology for the conversion of biomass into charred material; however pyrolysis can be further segregated into several types including slow, fast, vacuum, flash and microwave pyrolysis. Each process utilises different equipment and production conditions to maximise

individual products and properties. An indication of the difference between the various types of pyrolysis is demonstrated in Figure 1-2, comparing the process and product distribution from 'slow', 'intermediate', 'fast' pyrolysis and 'gasification'.

Process	Liquid (bio-oil)	Solid (biochar)	Gas (syngas)
FAST PYROLYSIS Moderate temperature (~500 °C) Short hot vapour residence time (<2s)	75% (25% water)	12%	13%
INTERMEDIATE PYROLYSIS Low-moderate temperature, Moderate hot vapour residence time	50% (50% water)	25%	25%
SLOW PYROLYSIS Low-moderate temperature, Long residence time	30% (70% water)	35%	35%
GASIFICATION high temperature (>800 °C) Long vapour residence time	5% tar 5% water	10%	85%

Figure 1-2: Differences in production conditions applied and resulting product yields obtained for various types of pyrolysis (Bridgwater, 2006; IEA, 2006).

The desired end products and application of these products is the determining factor for the selection of thermo-chemical treatment. Slow pyrolysis or conventional carbonization utilise lower heating rates to moderate temperatures (<700^{o}C), and long vapour residence times to generate higher char yields than other variations of pyrolysis (Brownsort, 2009; Verheijen *et al.*, 2009; Manyà, 2012). Slow pyrolysis is therefore regarded as the more favourable technology to maximise biochar yield for soil application while also generating valuable co-products for heat and power generation. However, if the generation of power is the desired outcome of the pyrolysis system then gas and liquid products are favoured over solid production. Fast pyrolysis is designed to rapidly heat biomass (>200 K min^{-1}) to peak temperature in a very short time scale resulting in short vapour residence times (< 2s). These conditions are designed to favour the formation of bio-oil while also inhibiting char formation (Brownsort, 2009; Manyà, 2012). The reaction conditions do not just affect the yield of products but also influence other properties such as

composition, viscosity, heating value etc. Although 'fast' and 'slow' pyrolysis are the leading routes for bio-oil and biochar production respectively, alternative methods for biomass conversion such as gasification, intermediate pyrolysis, flash pyrolysis and microwave pyrolysis also exist, with their own specific advantages and disadvantages.

Slow pyrolysis technology is optimized for biochar production to take advantage of the carbon sequestration and soil enhancing benefits that make biochar essential to realising carbon negative fuels. However biochar production is also associated with a reduction in energy output compared to biofuel production through fast pyrolysis (Gaunt & Lehmann, 2008), and therefore biochar's objective of sequestering C comes at a cost of diminished biofuel output (Jeffery *et al.*, 2013). Further understanding of the energy pathways to assess this trade-off between energy and biochar production is vital to the future consideration of slow pyrolysis technologies over alternative thermo-chemical treatments.

1.3.3 **Pyrolysis co-products**

Laird (2008) described biochar production as a 'win-win-win' strategy because of the co-production of energy rich products for use as biofuels. Pyrolysis can be used to transform low density organic materials into high energy density liquids known as bio-oil (~17 MJ kg^{-1}), a high energy density solid known as biochar (~18 MJ kg^{-1}) and a relatively low energy density gas known as syngas (~6 MJ kg^{-1}) (Mohan *et al.*, 2006; Laird *et al.*, 2009). The heating value of chars are comparable with lignite and coke while the heating values of bio-oil and pyrolysis gases are much lower than that of petroleum fuels and natural gas respectively (Yaman, 2004; Laird *et al.*, 2009). Although biochar has high energy content, in many cases its more beneficial application is incorporation into soil to increase the long term storage of carbon while reducing GHG and providing soil amendment benefits (Shackley & Sohi, 2010; Sohi *et al.*, 2010). Biochar can also be used to provide additional heat to the pyrolysis system through combustion (Yoder *et al.*, 2011; Bridgwater, 2012); however Woolf *et al.* (2010) described how the mitigation impact of biochar is about 25 % larger, on average, than the impact obtained if the same biomass was fully

combusted for energy. When additional benefits of biochar, such as increased plant growth, reduced N_2O emissions etc., are considered then biochar production could be a favourable option compared to the combustion of biomass or production of bio-oils (Hammond *et al.*, 2011). The formation, composition and potential applications of these co-products are discussed in the following section.

1.3.3.1 Liquid products

Pyrolysis liquids are created via rapid and simultaneous depolymerisation and fragmentation of cellulose, hemicelluloses and lignin following intense heating and are separated from the gas stream through rapid cooling (Czernik & Bridgwater, 2004; Mohan *et al.*, 2006). The properties of bio-oil are largely dependent on its chemical composition which is closer in origin to the elemental composition of its parent biomass that to that of petroleum oils. The main reason for the differences experienced between pyrolysis oils and hydrocarbon fuels are due to the presence of oxygen in the majority of the 300+ compounds that have been identified in bio-oil (Czernik & Bridgwater, 2004; Mohan *et al.*, 2006). These compounds consist of very complex oxygenated hydrocarbons and species such as: carboxylic acids, alcohols, ketones, phenols, alkenes, syringols, sugars etc. (Czernik & Bridgwater, 2004; Mohan *et al.*, 2006; Bridgwater, 2012). The high oxygen content has a direct effect on the energy density of bio-oil (50 % of that of conventional fuel oils) while also causing instability and immiscibility with hydrocarbon fuels. However continuing to increase the severity (HTT, heating rate, residence time etc.) of pyrolysis can lead to the cracking of vapours and formation of gases resulting in a reduced organic liquid yield with less oxygen (Czernik & Bridgwater, 2004).

Similarly to petroleum feedstock, bio-oil can also be used for the synthesis of chemicals with high and comparable revenue to energy and fuel products (Bridgwater, 2006, 2012; Mohan *et al.*, 2006; Isahak *et al.*, 2012). Such treatments are known as upgrading and consist of filtration, solvent addition, and hydrotreating as well as various forms of catalytic and vapour cracking (Bridgwater, 2012). Being a liquid, bio-oil can be easily stored and transported at lower costs compared to higher density biomass. However, variability in composition, high viscosity, poor

volatility, and corrosiveness are all challenges which have currently limited the expansion of the bio-oil market.

1.3.3.2 Gaseous products

Following the removal of the condensable liquids from the vapour stream the remaining non-condensable gases can also be burned directly for heat and power generation (Becidan *et al.*, 2007; Laird *et al.*, 2009; Yoder *et al.*, 2011). Pyrolysis gas consists of varying amounts of carbon monoxide (CO) (16 – 51 %) and hydrogen (H_2) (2 – 43 %) as well as CO_2 (9 – 55 %), methane (CH_4) (4 – 11 %) and small amounts of C_2 hydrocarbon gases such as ethane (C_2H_6) (Brownsort, 2009). Depending on the production parameters chosen for pyrolysis, the yield and composition of pyrolysis gas can change greatly, with the greatest volume and energy content produced by flash pyrolysis. Pyrolysis gas can be directly combusted, or cleaned and upgraded for use as a fuel source in turbines, as well as serving as an intermediate for the formation of other chemicals such as synthetic petroleum. However, the most common application is for self-sustainable pyrolysis by redirecting the pyrolysis gas back into the system to fulfil power or drying requirements (Becidan *et al.*, 2007; Laird *et al.*, 2009; Yoder *et al.*, 2011). One issue with pyrolysis gas is the low heating value, which restricts its uses as an efficient replacement for fossil fuel independently; but these problems could be rectified if the gas is used in combination with other fuels, or cleaned to remove the non-combustible fraction of CO_2(Chen *et al.*, 2012). Rather than designing the pyrolysis process to maximise the yield of one single product, the efficiency of biomass conversion in different socio-economic contexts can be improved through the co-production of solid char, liquid bio-oil and pyrolysis gas (Chen *et al.*, 2012).

1.3.4 Production parameters

The value and application of biochar heavily depends on its quality, composition, and physical, chemical and functional properties. All of these are dramatically altered by the pyrolysis conditions under which biochar can be produced. Furthermore, the production conditions not only influence biochar characteristics but also the energy content, composition and application of the liquid and gas co-products formed

alongside biochar. The main object of the PhD was to better understand how production conditions influence the final properties of biochar, and from this the agronomical and energy benefits of biochar production. However the task of investigating every possible production parameter would be too much for any project. Therefore a selection was made from the most frequently studied conditions and the importance of these variables are described briefly in the following section. Temperature is by far the most studied production variable, while heating rate, residence time and carrier gas flow rate are covered to a lesser extent, with the majority of the studies focusing on fast pyrolysis application rather than slow pyrolysis.

1.3.4.1 Feedstock

Feedstock is undoubtedly one of the most influential production conditions involved in pyrolysis. The starting material can define the properties of biochar as well as pyrolysis liquid and gas fractions. The chemical composition of biomass is very different when compared to that of coal, oil etc. due to the large proportion of oxygen present in plant carbohydrate polymers; meaning that pyrolytic chemistry differs greatly from fossil feeds. Biomass consists of three main components of natural polymeric materials: cellulose, hemicelluloses and lignin (Demirbas, 2000; Demirbas & Arin, 2002; Mohan *et al.*, 2006; Brown, 2009). Additional components are grouped as minerals (inorganic compounds) and extractives (small organic molecules or polymers) (Demirbas & Arin, 2002; Mohan *et al.*, 2006). The fractions of these components vary between feedstocks; however, exactly how the variation of these components influences important biochar properties such as stability is still relatively unknown.

Cellulose is a major constituent of biomass and in general can be considered to be 40 – 50 wt. % of the total biomass. It is a high-molecular-weight linear polymer consisting solely of glucose molecules. The crystalline structure of cellulose utilizes intramolecular and intermolecular hydrogen bonding allowing it to withstand decomposition better than hemicelluloses. At pyrolysis temperatures between 240 – 350^{o}C the dominant reaction is the degradation of cellulose to the more stable

anhydrocellulose and levoglucosan (Mohan *et al.*, 2006; Brown, 2009). Formation of anhydrocellulose follows an exothermic pathway yielding char and non-condensable gases, while levoglucosan is created through an endothermic devolatilisation process, leading to either tarry vapours or char (Di Blasi, 1998; Brown, 2009). Hemicellulose (also known as polyose) is the second major chemical constituent in wood with a rough concentration of 25 – 35 wt. %. The number of connecting units in hemicelluloses is only ~150 saccharide monomers, compared to 5000-10000 cellobiose units found in cellulose, thus accounting for hemicelluloses' lower molecular weight. Hemicellulose reacts more readily than crystalline cellulose and undergoes thermal decomposition between 200 – 260^{o}C, giving rise to more volatiles, and less char and tars than cellulose (Di Blasi & Lanzetta, 1997; Demirbas & Arin, 2002; Mohan *et al.*, 2006). Lignin is the third major component of wood accounting for 23 – 33 wt. % in softwoods and 16 – 25 wt. % in hardwoods. It has no exact structure and consists of an amorphous cross-linked resin. Lignin is a highly branched, polyphenolic substance with the chemical and physical properties of lignin changing depending on the type of feedstock as well as the isolation and extraction technology used to remove it from biomass. Therefore because lignin is altered during isolation, the thermal studies carried out on lignin may not accurately represent its behaviour in biomass (Mohan *et al.*, 2006).The decomposition of lignin begins at around 280^{o}C, with a maximum rate occurring between 350^{o}C and 450^{o}C, with the reaction proceeding to completion around 500^{o}C (Demirbas & Arin, 2002; Mohan *et al.*, 2006). Some studies have shown the decomposition of lignin to still be occurring at temperatures as high as 900^{o}C; however the individual decomposition rate of lignin may not be the same in biomass samples (Orfao *et al.*, 1999). Biomass with higher lignin content has been found to give a higher char yield, reflecting the fact that lignin preferably forms char during pyrolysis (Antal & Grønli, 2003; Demirbas, 2004). As the pyrolysis temperature is increased, additional structural modifications occur through the condensation of aromatic compounds and loss of functional groups via demethylation and decarboxylation reactions (Novak & Busscher, 2013). The breaking of C-O bonds during pyrolysis produces two competing reactions: depolymerisation of the chains and scission reactions within

carbohydrate molecules (Di Blasi, 1998; Mohan *et al.*, 2006; Demirbas, 2007). The monomer molecules produced by the polymerization undergo condensation reactions as they diffuse out of the particles or come into contact with the hot char surface forming more char, whereas the scission reaction forms a pyrolysis gas mixture of CO, CO_2, H_2, CH_4 and water (Mohan *et al.*, 2006; Demirbas, 2007).

As biochar is produced from plant materials; it is highly expected to contain varying amounts of plant macro nutrients (phosphorus (P), potassium (K), nitrogen (N), magnesium (Mg), calcium (Ca) etc.) and micro nutrients (iron (Fe), copper (Cu), sodium (Na), zinc (Zn), chlorine (Cl) etc.) (Chan & Xu, 2009; Lehmann *et al.*, 2011) retained within the biochar ash fraction. The concentration of ash is usually classed as the material remaining after the organic matter has been burned off (Mohan *et al.*, 2006; Enders & Lehmann, 2012). The mineral content has been shown to have a catalytic effect on the reactions occurring during pyrolysis and thus affecting the product yields and composition such as reactivity and ignition properties of chars (Antal & Grønli, 2003; Brown, 2009; Enders & Lehmann, 2012). Some studies have shown that increased concentrations of minerals such as K and Ca can result in higher char yields, as well as de-ashing methods leading to a fall in char yields due to removal of alkali metals which act as catalysts for char formation (Raveendran *et al.*, 1995; Antal & Grønli, 2003). Finally, the fifth wood component is comprised of organic extractives regarded as intermediates in metabolism as well as energy carriers. These extractives include waxes, gums, resins, starches, fats, proteins, simple sugars, pectins, phenolics etc. (Mohan *et al.*, 2006).

The feedstock composition is not the only important property related to the original starting material which could influence the final properties of pyrolysis co-products. The particle size of biochar is highly dependent on the nature of the original material and can have a considerable effect on the decomposition chemistry during pyrolysis (Antal & Grønli, 2003; Luo *et al.*, 2010). The size of particle needed can be related to the type of pyrolysis being applied with smaller particles needed during fast pyrolysis to allow for the high heating rates to allow for adequate heat and mass transfer of the pyrolysis reactions (Downie *et al.*, 2009). Slow pyrolysis can be

associated with the use of larger particles due to the use of slower heating rates. Large biomass particles have been associated with higher char yields due to the formation of secondary char as a result of volatile material being unable to rapidly escape from thicker particles (Antal & Grønli, 2003; Demirbas, 2004; Luo *et al.*, 2010). Therefore as particle size is reduced the volatile matter released is increased resulting in increased liquid and gas yields (Demirbas, 2004; Luo *et al.*, 2010). Hence using larger biomass particles would be beneficial for targeting char production while small particles would aid in the recovery of liquid products. The dynamics of feedstock are important when deciding the duration of pyrolysis with smaller particles allowing a faster rate of heat transfer and therefore accelerating the pyrolysis process (Luo *et al.*, 2010).

In addition to the mentioned feedstock properties the pre-treatment and post-treatment of biomass can also influence the final properties of co-products. Some of these processes include pelletizing, drying, acid washing, torrefaction, nutrient addition etc. however these were not considered for investigation under the scope of this PhD.

1.3.4.2 Highest treatment temperature

HTT has been shown to play a major role in the final yield, quality control and properties of pyrolysis co-products (Williams & Besler, 1996; Antal & Grønli, 2003; Manyà, 2012; Angin, 2013; Crombie *et al.*, 2013) with some researchers believing the selection of peak temperature to be the dominant variable in property development (Antal & Grønli, 2003; Crombie *et al.*, 2013). For example, it has been widely demonstrated by various researchers that increasing the reaction temperature results in decreasing biochar yields (as shown in Figure 1-3) while increasing both the liquid and gas concentrations.

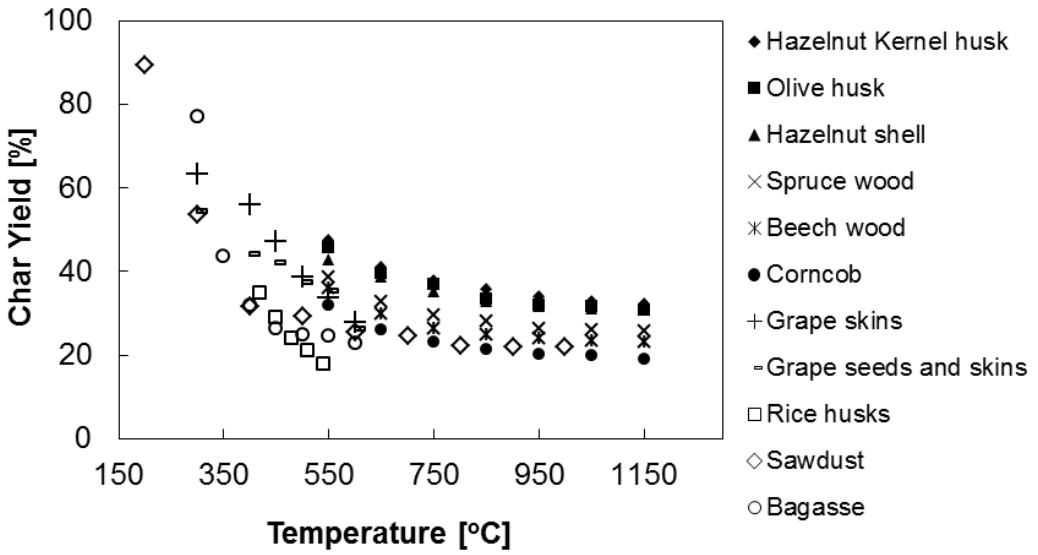

Figure 1-3: Combination of literature data showing the effect of temperature on char yield. Data obtained from Hazelnut Kernel husk, Olive husk, Hazelnut shell, Spruce wood, Beech wood, Corncob (Demirbas, 2001); Grape Skins, grape seed and skins (Xu *et al.*, 2009)**; Rice husk (Ji-lu, 2007); Sawdust (Valenzuela-Calahorro, 1987) and Bagasse** (Asadullah *et al.*, 2007)**.**

As the pyrolysis HTT increases, biomass undergoes a greater degree of decomposition, promoting the release of volatile material and resulting in decreased biochar yields (Demirbas & Arin, 2002; Mohan *et al.*, 2006; Enders *et al.*, 2012). Although the yield of biochar decreases with temperature, the proportion of emitted volatile material is increased, leading to a higher carbon/fixed C to char content of biochar (Williams & Besler, 1996; Demirbas, 2004; Gheorghe *et al.*, 2009; Enders *et al.*, 2012; Crombie *et al.*, 2013; Mašek *et al.*, 2013a, 2013b).

The results of the elemental analysis indicate that the C content of the char increases with pyrolysis temperature (inversely to char yield) through the release of N, H and O in volatile matter. The loss of O and H can be attributed to the scission of weaker bonds within the char structure, such as alkyl-aryl ether bonds brought on by increasing temperatures (Demirbas, 2004; Mohan *et al.*, 2006). Demirbas (2004) clearly illustrated a trend between the reaction temperature and C/O content of the char (Figure 1-4).

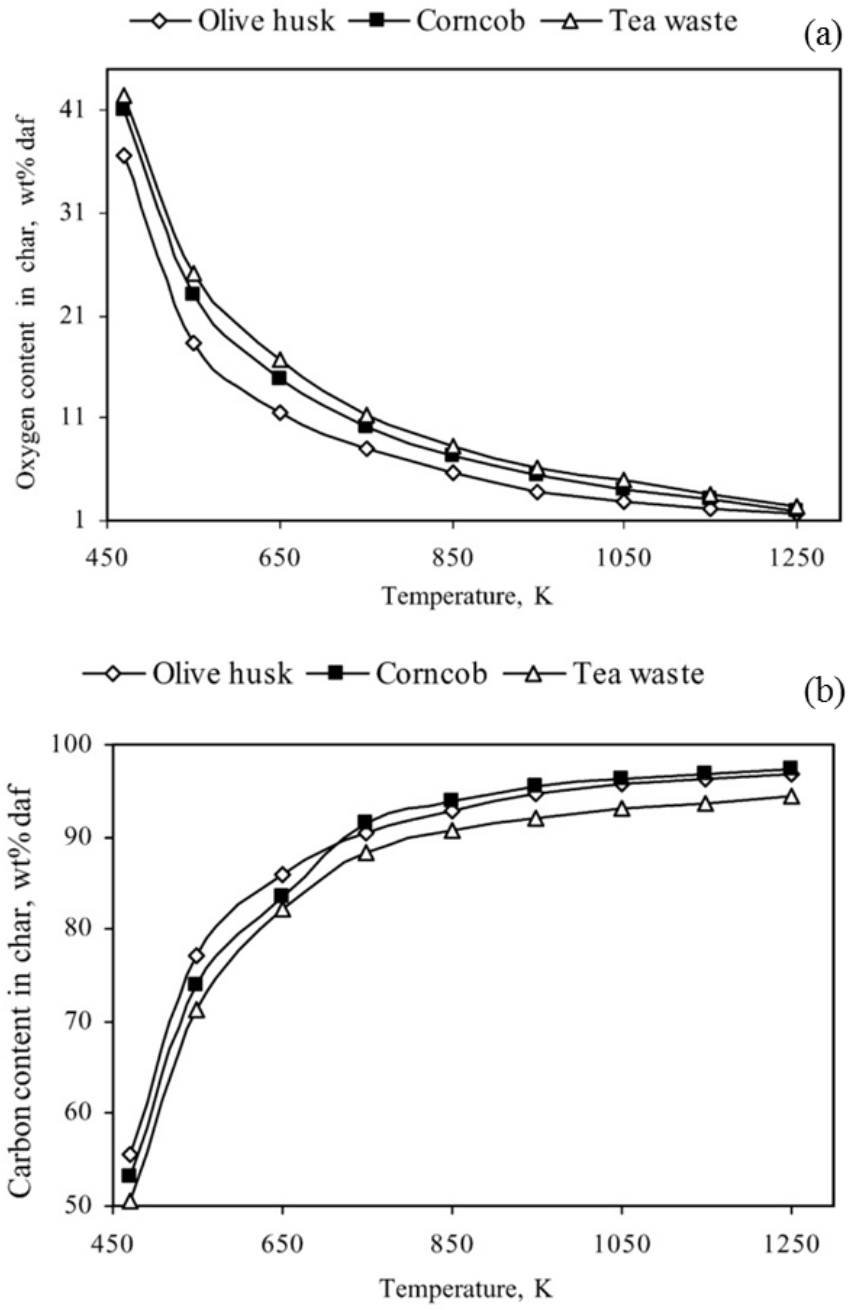

Figure 1-4: The effect of temperature on the (a) oxygen content and (b) carbon content of bio-char (Demirbas, 2004).

As the pyrolysis HTT continues to increase, so too does the release of volatile matter, and therefore the yields of liquid and gas products would be expected to rise. However, many studies have shown that as HTT approaches 500^{o}C the liquid yield reaches a limit. This is likely to be due to the increased occurrence of secondary

cracking reactions converting liquid volatiles into gas around 500^{o}C (Chen *et al.*, 2003; Phan *et al.*, 2008; Duman *et al.*, 2011; Fu *et al.*, 2011). Below the liquid yield peak temperature the gas yields are low and have varying dependence on temperature, however above the liquid yield peak temperature the gas yield rapidly increases as the main products of vapour decomposition are in gaseous form (Brownsort, 2009). The HTT applied during pyrolysis can also strongly influence properties such as surface area, pore structure, energy content, contaminants and the adsorption properties of the char product (Antal & Grønli, 2003; Bridgwater, 2006). Some of these properties are investigated further within the scope of the thesis.

1.3.4.3 **Heating rate**

The rate at which biomass is heated to HTT during pyrolysis is referred to as the heating rate. Researchers (Antal & Varhegyi, 1990; Zanzi *et al.*, 1995; Williams & Besler, 1996; Antal & Grønli, 2003; Becidan *et al.*, 2007; Isahak *et al.*, 2012; Angin, 2013) have continuously demonstrated that by decreasing the rate of heating the yield of char can be increased. As the heating rate is decreased an asymptote is achieved below which a decrease in rate of heating has no effect on the yield of char produced (Antal & Varhegyi, 1990). By increasing the heating rate the speed of progression through the degrees of biomass degradation is accelerated, leading to a rapid release of volatiles causing almost simultaneous breakdown of biomass components and increased reactions between char, liquid and gas products (Demirbas, 2004; Becidan *et al.*, 2007; Isahak *et al.*, 2012; Angin, 2013). Several studies have also shown that when using high heating rates above 500^{o}C, secondary cracking reactions of vapours and char favoured the formation of gas products rather than that of liquids (Williams & Besler, 1996; Tsai *et al.*, 2006; Sensöz & Angin, 2008; Isahak *et al.*, 2012). While low heating rates can provide sufficient time for good heat transfer between biomass particles, the application of higher heating rates is more realistic in a commercial pyrolysis unit to minimize production time. Therefore a comparison between different heating rates can provide an interesting insight into regions where large changes in biochar properties might take place.

1.3.4.4 Residence time (holding time)

Residence time refers to the amount of time that biomass spends within the chosen peak temperature range. The residence time of both the solid residue and the hot vapour produced during pyrolysis conditions can both largely affect the proportions of product yields (Verheijen *et al.*, 2009). Investigations into the influence of residence time during slow pyrolysis are limited. The fundamental differences between different types of pyrolysis come down to their temperature range and particle residence time (Bahng *et al.*, 2009). For example, slow pyrolysis operates with a particle residence time of minutes to hours, while fast pyrolysis is on a much shorter scale of seconds to minutes (Bahng *et al.*, 2009; Verheijen *et al.*, 2009; Manyà, 2012).

Ronsse *et al.* (2013) and Gheorghe *et al.* (2009) found that during slow pyrolysis, increasing the severity of pyrolysis (HTT and residence time) resulted in increased release of volatiles, thereby reducing char yield and increasing the concentration of fixed C within biochar. The residence time was also seen to influence the elemental composition of the final biochar product as well as the calorific value, with a higher heating value as residence time was extended. Wannapeera *et al.* (2011) discovered that by increasing the holding time at selected temperatures the torrefied biomass contained a higher carbon content and calorific value, while also decreasing the tar yield produced during torrefaction. Residence time has also been connected to changing the extent of physical and chemical alterations which occur during biomass pyrolysis (Verheijen *et al.*, 2009). However some studies have shown no effect of residence time on char yield, which may account for the limited number of investigations into the impact of this production variable (Shen & Gu, 2009; Agrafioti *et al.*, 2013). The influence of residence time on the properties of biochar is severely under researched and therefore there is high demand for a detailed study from the point of view of slow pyrolysis.

1.3.4.5 Vapour-phase residence time (carrier gas flow rate)

The vapour-phase residence time refers to the amount of time that vapours released from biomass during pyrolysis are present to undergo reactions within the hot zone

before being swept away by carrier gas. This time can be altered by changing the flow rate of carrier gas which fills the system. Increasing the carrier gas flow rate can decrease the duration of contact the primary vapours released during pyrolysis will have with the hot surfaces of char, reducing secondary char formation and therefore generating lower char yields (Encinar *et al.*, 2000; Antal & Grønli, 2003; Tsai *et al.*, 2007; Sensöz & Angin, 2008; Xu *et al.*, 2009; Demiral & Ayan, 2011; Demiral *et al.*, 2012; Hu *et al.*, 2013). This could then result in increased liquids and gas concentrations. Fast pyrolysis operates with high gas flow rates, so that the vapours released during pyrolysis are flushed away from any potential sites of secondary char formation as soon as possible (Demiral & Ayan, 2011) to maximise the collection of liquid products (Bridgwater, 2004; Yaman, 2004; Sensöz & Angin, 2008; Hu *et al.*, 2013). The use of long residence times in conjunction with high temperatures favours the release of gas during pyrolysis, while lower temperatures and shorter vapour residence times results in higher liquid yields (Tsai *et al.*, 2007; Bridgwater, 2012).

Other potential reaction conditions that can be applied during pyrolysis can include the use of catalysts, pressure, introduction of steam or other selected gas flows for activation, pre-treatment of feedstock, and post treatment of biochar. These production parameters can also dramatically change the properties of products generated by pyrolysis but will not be discussed within this thesis. So far research has been focused on the characterisation of biochar through quantifying physical and chemical properties, with few to no studies or techniques designed for analysing biochar for important functional properties. The focal point of biochar analysis has started to shift towards this area over recent years as it becomes apparent that determining properties responsible for the response of biochar in the environment is crucial to its success as a soil amendment and carbon sequestration material. This research makes a significant contribution to this effort through the analytical screening of biochar samples to reduce the potentially limitless varieties of biochar and to focus on improving key functional properties of biochar related to its environmental performance.

1.4 Biochar functional properties

The best way to determine the effect of biochar in the environment is through field experiments measuring the response of biochar over a long time period as there are numerous variables in the environment which cannot be accounted for within a laboratory environment. However although large scale trials are underway worldwide the results can take months, even years to become apparent. Therefore urgent research is needed into the design and implementation of short term laboratory methods for quantitative or at least qualitative measurements of the important functional properties of biochar related to its response in soil. Biochar has shown several properties which have resulted in a positive response to the environment. Some key properties have been identified and described in the following section.

1.4.1 Carbon sequestration

Biochar's environmental stability is a key property towards achieving its potential to mitigate climate change through sequestering atmospheric CO_2 for long periods of time while also reducing GHG emissions (Jeffery *et al.*, 2013). Biochar is considered as part of the black C continuum along with other by-products of combustion such as charcoal, soot, graphite etc. (Baldock & Smernik, 2002; Masiello, 2004; Liang *et al.*, 2008). Black C , through the use of C-14 dating, has been found to be the oldest C fraction in soil, displaying stable components with MRTs of several thousand years (Preston & Schmidt, 2006; Liang *et al.*, 2008; Lehmann *et al.*, 2009). However there remains a lot of uncertainty over the timeframe under which C will remain sequestered, due to variation in biochar properties stemming from the number of feedstock types and processing conditions available. The C sequestration potential of biochar could be divided into two measures of C: stored carbon and emitted carbon. The largest chemical difference between biochar and other organic material is the higher proportion of aromatic C and fused aromatic C structures. This fused aromatic structure can have varying forms including turbostratic C, which forms at high temperatures and amorphous C, which dominates at lower pyrolysis temperatures

(Lehmann *et al.*, 2011). The high stability of biochar is derived from the nature of these C structures.

Although having high levels of biological and chemical resistance, biochar is still gradually mineralized to CO_2; otherwise, SOM would be dominated by biochar accumulated over long time scales (Kuhlbusch & Crutzen, 1995; Masiello, 2004; Cheng *et al.*, 2006). Therefore the longevity of biochar in soil cannot be quantified by one number, as biochar is not one consistent homogeneous state (Hedges *et al.*, 2000). Assessing the longevity of biochar is not the only property of interest when stability is concerned, the sometimes forgotten component of labile-C content (defined as carbon readily accessible to soil microbes) within biochar also plays an important role in the assessment of the short term recalcitrance of biochar and should be quantified. After low temperature pyrolysis, biochar may contain an unconverted or partially converted biomass fraction which, on addition to soil, is rapidly mineralized resulting in a turnover time between weeks and decades (Hamer *et al.*, 2004; Cheng *et al.*, 2006; Hammes *et al.*, 2007; Novak *et al.*, 2010; Bruun *et al.*, 2011; Calvelo Pereira *et al.*, 2011; Jones *et al.*, 2011; Biederman & Harpole, 2013). This mineralization results in a small short term CO_2 flux (Zimmerman, 2010; Bruun *et al.*, 2011; Calvelo Pereira *et al.*, 2011; Cross & Sohi, 2011; Jones *et al.*, 2011) and could be responsible for mineralization of other soil C (Hamer *et al.*, 2004; Cross & Sohi, 2011; Jones *et al.*, 2011; Lehmann *et al.*, 2011; Zimmerman *et al.*, 2011). In many cases the observed release of CO_2 from biochar takes place over a relatively short period of weeks or months before dissipating (Smith *et al.*, 2010; Jones *et al.*, 2011) however the short-term losses of native SOM will be smaller than the C gain of biochar and might be insignificant (Woolf & Lehmann, 2012).

Different fractions of biochar will decompose at different rates under different conditions determined by method of production, starting material, climate and soil properties. This makes the quantification of long term as well as short term biochar stability extremely important to the environmental and economic feasibility of biochar production. Direct measurements of this stability on the timescale of decades or even a century is not possible, leading to the necessity for development of rapid

assessment tools for screening fresh biochar. During the evaluation of biochar stability, the total C, fixed C as well as elemental ratios have been most commonly used to assess the stable fraction of biochar C. However new tools are being developed (Hammes *et al.*, 2007; Cross & Sohi, 2011, 2013; Harvey *et al.*, 2012) to better measure the environmentally stable fraction of biochar.

1.4.2 **pH**

Biochar can be manufactured at almost any pH between 4 and 12 by appropriate choice of feedstock and pyrolysis conditions (Lehmann, 2007). Studies have shown that at less severe pyrolysis conditions more labile and oxygenated carbon with high acid-base surface functional groups are retained by the char, generating low pH biochar. However, as the severity of pyrolysis is increased, more acidic groups (e.g. carboxyl) have become deprotonated, consequent causing a rise in the pH of biochar in solution (Chan & Xu, 2009; Ronsse *et al.*, 2013; Zheng *et al.*, 2013). Enders *et al.* (2012) suggested that a large proportion of the ash in high-ash feedstock contains carbonates. These carbonates have been associated with having a liming effect on soil acidity thus increasing the soil pH following addition of biochar (Glaser *et al.*, 2002; Novak *et al.*, 2009; Shackley & Sohi, 2010; Van Zwieten *et al.*, 2010; Biederman & Harpole, 2013). Biochar of an alkaline nature has been shown to increase microbial activity in acidic soils through increasing the soil pH as well as CEC (Rondon *et al.*, 2007; Verheijen *et al.*, 2009; Atkinson *et al.*, 2010; Van Zwieten *et al.*, 2010; Rajkovich *et al.*, 2011; Biederman & Harpole, 2013; Liu *et al.*, 2013) while the effect was not as large when applied to alkaline soils (Van Zwieten *et al.*, 2010; Biederman & Harpole, 2013). Increasing the alkaline nature of biochar can improve the effectiveness of improving crop productivity however a number of variables such as soil type and climate could influence the soil fertility. Furthermore, applying biochar with too high a pH can also have negative effects on soil as a result of a micronutrient deficiency (Chan & Xu, 2009).

1.4.3 **Nutrient retention**

Many studies have reported biochar's effectiveness at improving soil quality and crop production (Lehmann *et al.*, 2006; Liang *et al.*, 2006; Laird, 2008; Atkinson *et al.*, 2010; Van Zwieten *et al.*, 2010; Jeffery *et al.*, 2011; Rajkovich *et al.*, 2011; Spokas *et al.*, 2012; Biederman & Harpole, 2013; Liu *et al.*, 2013). Of these studies a limited number investigate how production conditions can influence the nutrient composition of biochar (Zheng *et al.*, 2013) as biochar is manufactured from biomass (virgin and non-virgin) and is therefore expected to contain high C concentrations as well as plant macro nutrients (phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca) etc.) and micro nutrients (iron (Fe), copper (Cu), sodium (Na), zinc (Zn), chlorine (Cl) etc.) (Chan & Xu, 2009; Lehmann *et al.*, 2011). Removal of biomass from its habitat for biochar production can leave the soil deprived of nutrients, which is why reapplying biochar back to the soil helps return the majority of these nutrients to the soil from which they came (Laird *et al.*, 2010). However the total concentration of nutrients within biochar is not an appropriate indicator of the bioavailability of nutrients (Chan & Xu, 2009; Spokas *et al.*, 2012) since only a small fraction of the total content is immediately available.

The positive response from application of biochar to soil could be due to a host of potential reactions related to biochar such as retention of soil nutrients, removal of soil constraints limiting plant growth (increasing soil pH), toxin neutralisation, enhanced soil physical properties (water retention), reduced soil strength, improved N fertilizer-use efficiency and CEC (Chan & Xu, 2009; Van Zwieten *et al.*, 2010). Biochar per unit of carbon has a much greater ability than that seen for soil, SOM and clay for absorbing cations (e.g. Ca^{2+}, K^{+}, NH_4^{+}, Mg^{2+}) partially due to the combined effect of larger surface area, greater charge density and increased negative surface charge affected by the pyrolysis conditions (Sohi *et al.*, 2010; Yuan *et al.*, 2011; Manyà, 2012). This trend is used to propose that biochar can act as a binding agent in soil by improving the soil's ability to adsorb and retain cations (e.g. Ca^{2+}, K^{+}, NH_4^{+}, Mg^{2+}) (Chan & Xu, 2009; Major *et al.*, 2009; Manyà, 2012).

High variability of nutrient composition has led to large deviation in the plant and soil response following biochar addition. This can cause large questions over the optimal application rate as well as biochar type. Therefore the optimal application rate and applied biochar type could potentially be determined on a site basis due to the influence of plant and soil species. In order for the full potential of biochar to sequester C and provide agricultural benefits to be realized, it is necessary to rapidly assess biochar for key functional characteristics prior to large scale deployment. By improving our knowledge of the influence production conditions have on key biochar properties, improvements can be made to the pyrolysis process to refine the reproducibility and control of biochar production, with the ability to selectively engineer biochar properties being the desired end goal.

1.5 **Bespoke biochar**

Biochar properties are currently far from being consistently reproduced, which makes the application of biochar to soil not as simple as "a one-size fits all" principle. Research is therefore beginning to focus on biochar production tailored to target specific soil deficiencies which may vary with location (Czimczik & Masiello, 2007; Novak *et al.*, 2009; Sohi, 2012; Spokas *et al.*, 2012; Novak & Busscher, 2013).

Bespoke biochar is a concept under investigation by the UK Biochar Research Centre (UKBRC) which refers to biochar specifically engineered to deliver a particular function or combination of functions, such as maximum biological stability, maximum agronomic benefit, mitigation of trace gas emissions, etc. As some biochar properties reach a maximum at different temperatures, the process of optimising every property would be impossible (Jeffery *et al.*, 2013). Therefore the design of the production process could be to maximise a particular benefit and/or to minimise potential trade-offs. Some trade-offs are more obvious than others, such as biofuel vs biochar, virgin vs non-virgin feedstock and climate change mitigation vs soil fertility (Jeffery *et al.*, 2013). By collecting data on the influence of production conditions on biochar's energy and environmental properties, the efficiency and focus of the production process can be improved to enhance the application and

response of biochar in soil, while gaining a better understanding of the balance between important trade-offs.

The Lehmann group at Cornell University attempted to determine the optimum temperature for biochar production through monitoring how several properties changed with temperature, as shown in Figure 1-5 (Lehmann, 2007). Their results were used to identify a temperature region within which a 'combined maximum' of the different properties occurred.

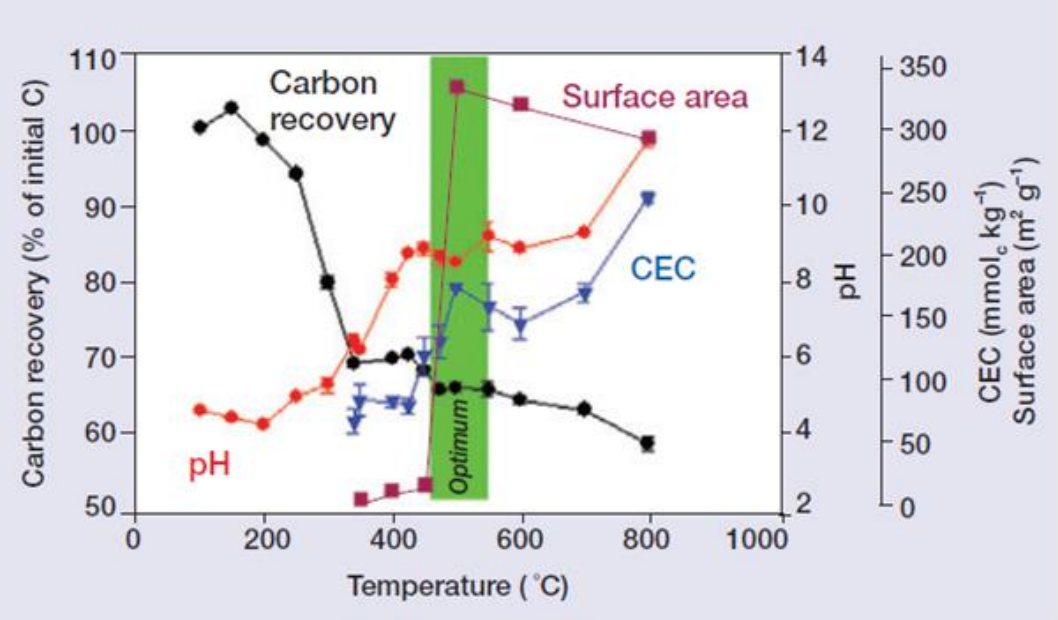

Figure 1-5: Dependence of biochar surface area, pH, CEC and carbon recovery on production temperature (Lehmann, 2007).

Although this study has made an initial attempt at optimising the temperature selection for biochar production there is a demand for further advancements of this type of study before the idea of bespoke biochar can truly start to take shape. Temperature is a crucial variable during pyrolysis; however there are several other production conditions which can also influence the final properties of biochar, not to mention the composition and energy value of the liquid and gas co-products, something not considered in the Lehmann study. Furthermore an essential property

not consideration in the Lehmann study is the effect of temperature on the environmental stability of biochar.

Improving the ability to control the final properties of biochar to enhance its agronomical and C mitigation benefits is the first step towards manufacturing bespoke biochar. However the trade-offs between biofuel production, C sequestration and soil enhancement could all impact the focus of the overall pyrolysis system, influencing the production condition selection, and therefore should be considered during bespoke biochar production. There is clearly a high necessity for research into the impact of key soil processes on biochar produced from a systematic set of production conditions. This would begin to generate definitive conclusions on the effect production conditions have on biochar's properties and what response this could lead to in field applications (Shackley & Sohi, 2010). Optimising the pyrolysis process does not necessarily mean finding a zone where as many properties as possible peak but rather looking to find a desired balance between the key outputs of the system to generate a positive environmental response following the application of biochar.

1.6 **Context of thesis**

Pyrolysis biochar systems can be used to transform biomass into highly stable C capable of enhancing soil fertility, while producing renewable heat and electricity to offset fossil fuel emissions. However, to fulfil its potential, there is still considerable uncertainty surrounding biochar production and use which needs to be investigated. To date the characterisation of biochar has largely focused on quantifying physical and chemical properties, due to the ease and rapid turnaround of results associated with laboratory analysis. These physicochemical properties have then been extensively used to predict the behaviour of biochar in soil; however the concept of identifying and quantifying the important environmental properties of biochar, which determine its soil function, is relatively new. Although the best method for ultimately determining biochar's environmental response would be through large scale field trials, field trials are expensive and time consuming processes which provide

minimal results over a short time period. Therefore the use of rapid and robust assessment techniques for the screening of biochar samples could provide quick and important findings about new types of biochar. This could substantially improve the progression of biochar research through identifying important regions of property development and reducing the vast number of potential biochar types down to a selected few for advanced environmental trials. Gaining a better understanding of the effect production conditions can have on biochar will aid in refining the pyrolysis process to selectively improve specific biochar properties to maximise its performance in different locations. However engineering the process for the sole enhancement of the biochar product can have ramifications on the entire system, ultimately affecting the large scale feasibility of biochar production.

One of the biggest debates hindering the development of biochar production focuses on the trade-off between heat/power generation and carbon sequestration. Biochar competes for sustainable biomass resources, such as virgin and non-virgin biomass, with other alternative uses of biomass, e.g., for production of heat, power, chemicals and other materials. Therefore the generation and storage of biochar, whether in soil or elsewhere, has always been associated with the sacrifice of energy in favour of carbon storage. The co-production of bio-oil and gas alongside that of biochar increases the potential to mitigate C by providing alternative fuels to offset the high demand on fossil fuel energy, thereby reducing fossil-C emissions and adding to the proposed 1GtC reduction set out in the carbon and climate stabilisation triangle. The energy distribution between the pyrolysis co-products is determined by the production conditions and their influence on the degree of biomass degradation. The effect of production conditions on the energy balance of fast pyrolysis and gasification technologies has been well reported in literature, due to their growing importance as alternative energy technologies. However the majority of biochar publications are centred on the C mitigation and agricultural benefits related to biochar, with little consideration to the energy output of the pyrolysis system.

While C mitigation, soil enhancement and energy generation are all important outcomes of pyrolysis, no published research has tried to adjust the pyrolysis process

in an attempt to improve all three of these benefits or evaluate the balance between them. Therefore, this PhD has focused on improving the understanding of how production conditions impact the carbon mitigation and soil enhancement ability of biochar, while determining the influence that maximising these benefits may have on the energy balance of slow pyrolysis. Understanding the delicate balance between the conversion of biomass to heat/power or to biochar and what each outcome means for the pyrolysis system is a critical step towards the development of bespoke biochar.

1.7 Thesis objectives and aims

This thesis aims to investigate how production conditions impact the carbon mitigation and soil enhancement ability of biochar, as well as the energy balance of the production process (slow pyrolysis). From these objectives the thesis also aims to provide a better understanding of the trade-offs between the C sequestration, environmental functions and heat/power supply potential of slow pyrolysis to aid in the development of bespoke biochar. To address these aims, five principle objectives were set.

1. Investigate the impact of pyrolysis process conditions on biochar functional properties, with particular interest in the C sequestration potential of biochar.
2. Understand how varying the production conditions of pyrolysis affects the energy distribution between co-products, and from this the energy balance of the pyrolysis process.
3. Investigate the potential trade-offs between biofuel production, C sequestration and soil enhancement benefits of biochar.
4. Using the full data set of the thesis, study the potential for relationships between biochar properties and production conditions, to develop statistical models aimed at predicting biochar properties.
5. Explore the potential to produce a biochar product which could maximise a specific response or combination of responses, leading towards the realisation of bespoke biochar.

The layout of this thesis comprises of four individual paper chapters and one chapter not intended for publication, each of which addresses one or more of the objectives listed above. A detailed description of the materials used, experimental procedures and analysis performed throughout the thesis follows in Chapter 2. Chapters 3-7 address Objectives 1-5 with cross over between each chapter, while Objective 5 is addressed throughout the individual paper chapters but is mainly the focus of Chapter 8. In addition to the chapters displayed within the main body of the thesis, Appendix 2 and 3 also contributed to addressing Objectives 1 and 2.

Chapter 3 – Over recent years, several methods for assessing the stability of biochar have been proposed, however none of them have yet been recognised or validated for this purpose. These tests focus on using the analytical determination of the physicochemical properties of biochar to predict stability, rather than analysing the stability of biochar in the environment. Therefore this chapter investigated the effect that HTT, heating rate and feedstock selection had on biochar stability, determined by three techniques, addressing Objective 1. A systematic set of biochar samples were analysed for proximate analysis (technique 1), ultimate analysis (technique 2) and direct oxidation (technique 3), to assess the variation in biochar stability between each technique. Comparisons between stability on a biochar C basis and a feedstock C basis were used to investigate the overall C sequestration potential of biochar and the impact that varying production conditions has on this potential (Objectives 1 and 3). The specific aims of this chapter were:

- To observe the effect of selected production conditions on the biochar stability determined by proximate analysis, elemental analysis and direct oxidation;
- To determine the C sequestration potential of biochar by expressing biochar C stability on a feedstock C basis;
- To evaluate the relationship between the different stability assessment tools.

Chapter 4 – Building on Chapter 3, the impact of production conditions was further investigated on additional functional properties related to the soil enhancing benefits of biochar (labile-C content, pH, CEC and nutrient availability) as well as further studying the C sequestration potential (Objective 1). Through investigating both the soil amendment and C sequestration potential of biochar any potential trade-off between these two benefits can be assessed (Objective 3). A better understanding of possible trade-offs can help to refine the process conditions to maximise the environmental potential of biochar (Objective 5). The specific aims of this chapter were:

- To evaluate the impact of production conditions on specific biochar functional properties;
- To identify possible or impossible combinations of biochar functional properties.

Chapter 5 – The concept of storing C through biochar production has typically been associated with reduced liquid and gas co-products and thus a loss in heat/power output. Therefore this chapter investigates the influence that feedstock and production conditions (HTT, residence time and carrier gas flow rate) have on the amount of carbon (stable and non-stable) and energy stored in biochar, as well as the amount of available energy in pyrolysis liquids and gas. Through assessing the stability of biochar and energy output of the system it could be determined whether or not the pyrolysis system could simultaneously achieve high efficiency of biomass conversion to heat and/or power as well as high carbon storage, addressing Objectives 1, 2 and 3. The specific aims of this chapter were:

- To investigate the effect of HTT, residence time and carrier gas flow rate on the product energy distribution as well as the carbon sequestration potential of biochar;
- To determine how more intense pyrolysis conditions might impact the amount of carbon emitted during pyrolysis;

- To use this information to select pyrolysis conditions best suited to maximise both heat/power supply potential of slow pyrolysis and biochar stability.

Chapter 6 – During the production of biochar, liquid and gas streams could provide important economic benefits to the system. However the composition of the gas stream produced during slow pyrolysis has rarely been analysed since the majority of gas studies focus on fast pyrolysis and gasification systems. Therefore Chapter 6 brings together the composition analysis of all the pyrolysis gas produced during the experiments in Chapters 4 and 5. From these studies the final composition and energy content of the gas stream can be assessed, contributing to Objective 2. By determining the energy content of the pyrolysis gas, the extent to which the pyrolysis process can be maintained based solely on the gas stream can be investigated. Achieving a self-sustaining system could increase the availability of biochar to maximise the agronomic benefits of the pyrolysis system (Objective 3 and 5). The specific aims of this chapter were:

- To study the influence of feedstock, HTT, heating rate, residence time and carrier gas flow rate on the composition of the pyrolysis gas produced during biochar production;
- To evaluate whether or not the energy content of the pyrolysis gas stream was sufficient to maintain the pyrolysis process.

Chapter 7 – Feedstock is arguably one of the most important variables when determining the final composition and properties of biochar, bio-oil and pyrolysis gas since these are derived from the breakdown of cellulose, hemicellulose and lignin during pyrolysis. A vast number of different types of biomass have been used for biochar production, however the identification of relationships between the feedstock components (cellulose, hemicellulose, lignin and ash) and important biochar properties such as C stability and labile-C content is still absent from literature. By using the data collected within the previous chapters, statistical analysis can be

performed to look for potential statistical relationships between the production conditions and feedstock used during pyrolysis, and the final properties of biochar. The presence of statistical relationships can then be applied to produce statistical models which attempt to describe that relationship, and from this predict the properties of biochar, thus addressing Objective 4, while also testing the strength of these predictions. The specific aims of this chapter were:

- To analyse the full biochar data set looking for statistical relationships between properties;
- To design a linear regression model to attempt to predict biochar stability based on multiple production variables;
- To use the data set of chapter 5 to design a linear regression model for predicting the HHV of biochar.

Chapter 8 – This section brings together the major findings from the above chapters to address Objectives 1-5 and the primary aim of the thesis while assessing what these results means for the future development of biochar.

Appendix 2 – This section describes the work done as part of a joint project between the UKBRC and the University of York investigating the differences between biochar stability and the energy balance of the system, when using microwave pyrolysis compared to slow pyrolysis. From these studies the impact on biochar stability that the process conditions applied by both types of pyrolysis could be assessed, addressing Objective 1; while also gaining knowledge of the difference between each process and determine a preferred option. Furthermore, by comparing the energy balance of the systems, the trade-off between energy output and biochar production could be further investigated to contribute to Objective 2 and aid in determining the balance addressed in Objective 3.

Appendix 3 – This section describes the work done as part of a two month project undertaken by the candidate while at Cornell University. Through the analysis of a large biochar collection situated at Cornell, further data on determining the

environmental stability of biochar could be obtained. Therefore this study contributed to better understanding how the production conditions can influence the final C stability of biochar, and thus further help in addressing Objective 1.

Chapter 2. **Materials and Methodology**

2.1 **Repetition**

Due to repetition of the key equipment and methodology used in each chapter of this thesis, one all-encompassing section has been created to describe in detail the justification of pyrolysis conditions, setup of the pyrolysis system as well as the sample collection procedure and product analysis. The main variation in experimental set up between pyrolysis experiments was associated with the chosen production conditions and feedstock necessary to investigate the relevant hypotheses. Therefore the specific production conditions and feedstock used for each experiment are of most relevance to their corresponding chapters and therefore will be presented within each individual chapter.

2.2 **Feedstock**

The general strategy for the identification and resourcing of biomass for experiments was initially focused on utilising biomass with high global and European availability. However as obtaining international biomass such as sugarcane bagasse and rice husk proved increasingly difficult, due to the need of documentation for importation of foreign organic material, the project progressed focusing on biomass readily available in the UK such as wood pellets (4.1 Mt yr^{-1}), wheat straw (4.7 Mt yr^{-1}), oil seed rape (2.4 Mt yr^{-1}) and pine wood chips (Shackley & Sohi, 2010). It was believed that highly available biomass could prove a useful starting material to evaluate varying conditions for biochar production, due to the lower cost of feedstock compared to more specialised and harder to obtain biomass. The selection of biomass for pyrolysis was also based on obtaining materials with considerably differing structure and chemical composition. The individual chemical components within biomass significantly influence the composition of final pyrolysis co-products; and therefore finding the optimum combination of components such as cellulose, hemicellulose and lignin could generate the most favourable balance of biochar properties, such as stability or nutrient availability etc. However, biochar designed in

such a way will also come with the high cost associated with bespoke products designed for a specific purpose. While this type of biochar market would be feasible for high end clients, for biochar production on a local scale to remain affordable, feedstock selection would need to be based on the most available and cheapest source. Therefore the work of this thesis has both allowed for the development of a specifically engineered biochar project while also utilising highly available biomass.

2.3 Pyrolysis

2.3.1 Conditions

The conditions under which pyrolysis is performed can dramatically alter the final properties and composition of the solid, liquid and gaseous products obtained from the process. There is a large array of pyrolysis parameters which can influence the physical, chemical and functional properties of biochar such as HTT, heating rate, residence time, carrier gas flow rate, feedstock, particle size, gas environment, pressure, use of catalysts as well as pre-treatment (drying, chemical addition etc.) and post-treatments (crushing, storage, activation etc.). Due to time constraints of the PhD and available equipment, only a small number of conditions could be extensively investigated; therefore only feedstock, HTT, heating rate, residence time and carrier gas flow rate were chosen. The parameters of feedstock and heating profile (i.e. HTT and heating rate) have been frequently identified as the most important variables for determining the final composition and properties of biochar as well as bio-oil and pyrolysis gas (Williams & Besler, 1996; Antal & Grønli, 2003; Downie *et al.*, 2009; Angin, 2013). Furthermore, the importance of residence time and carrier gas flow rate during biochar production is less conclusive due to a limited number of studies varying these conditions. Therefore detailed investigations would aid in reaching a definitive conclusion on the importance and preferred value for these variables. Details of the selected process conditions under which biochar was produced are unique to each chosen hypothesis being studied and therefore are described within each chapter. A list of all feedstock used within this thesis was presented in Table 2-1, along with particle size, initial moisture content on receiving biomass and supplier.

The production conditions were altered to cover relatively low and high ranges to aid in the ease of identifying any clear influence of these conditions on the final properties of biochar, bio-oil and pyrolysis gas. The temperature range studied throughout the experimental work covered a range from 350^{o}C to 650^{o}C with 450^{o}C and 550^{o}C values serving as intermediate values. This temperature choice covered the main regions of biomass degradation as well as the respective upper and lower limits of temperatures associated with slow pyrolysis. Pyrolysis at HTTs below 350^{o}C would be considered to be torrefaction rather than pyrolysis while pyrolysis above 650^{o}C could have resulted in insufficient char yields required for analysis. For varying the heating rate of pyrolysis a relatively slow (5^{o}C min^{-1}) and medium (100^{o}C min^{-1}) rate of heating was again chosen to cover both ends of the spectrum. A low heating rate was selected to provide longer heating time in an attempt to provide adequate time for sufficient heat transfer and heat penetration into the biomass particles while the medium heating rate was selected to simulate conditions used for industrial-scale slow pyrolysis. The large continuous pyrolysis units at UKBRC were considered when determining which values to apply for heating rate and residence time. Based on realistic times seen in industrial sized units to generate fast conversion of feedstock to biochar, the residence times chosen were therefore 10, 20 and 40 minutes. This then allowed for future sample comparisons between small batch pyrolysis and medium-large scale continuous units. Finally, the standard flow rate of nitrogen (N_2) carrier gas through the pyrolysis system was initially calculated by Dr Peter Brownsort (UKBRC), based on the comparison of flow rate used in Ryu *et al.*, (2007), to provide a linear cold flow velocity within the empty pyrolysis tube of approximately 3 mm s^{-1} (0.33 $\pm$ 0.02 L min^{-1}) .This carrier gas flow rate was designed to provide a slow flow velocity to maximize vapour/solid interactions while remaining well within the pressure limits of the system. Therefore to investigate the effect that carrier gas flow rate would have on biochar properties the standard flow rate was either reduced to no flow rate (0 L min^{-1}) or doubled (0.66 $\pm$ 0.02 L min^{-1}).

Table 2-1: List of feedstock used in pyrolysis experiments throughout the PhD.

Feedstock	Short Form	Particle Size	Moisture [wt. %]	Aquired From
Pine Wood Chips	PC	ranging from 15 × 5 × 4 mm to 100 × 40 × 15 mm	4.5	Scottish Farm in East Lothian, Scotland
Rice Husk	RH	uniformly less than 5 × 4 × 1 mm particle size	4.3	Kameoka, Kyoto Prefecture, Japan
50/50 Wheat:Oilseed Rape Straw Pellets	SP	ø 6mm	5.4	StrawPellet Ltd., Rookery Farm, Lincolnshire, England
5/95 Pine:Spruce Softwood Pellets	WP	ø 6mm	10.6	Puffin Pellets, Aberdeenshire, Scotland
Wheat Straw	WS	primary fragments 10 × 3 × 1 mm to 90 × 5 × 4 mm	4.5	StrawPellet Ltd., Rookery Farm, Lincolnshire, England
Wheat Straw pellets	WSP	ø 6mm	13.3	StrawPellet Ltd., Rookery Farm, Lincolnshire, England

Table 2-2: Feedstock composition data on a dry weight basis (db).

	Biomass componenets [wt.% (db)]			Proximate analysis [wt.% (db)]			Ultimate analysis [wt.% (db)]						
Sample	Cellulose	Hemicellulose	Lignin	Ash	Fixed C	Volatile Matter	C	H	N	O	O:C	H:C	HHV [MJ/kg]
PC	52.0	21.0	12.6	2.0	22.3	75.7	50.7	4.8	0.0	42.4	0.6	1.1	19.0
RH	16.0	42.0	37.0	22.3	15.7	62.0	39.6	5.1	0.2	32.8	0.6	1.5	14.9*
SP	23.0	49.0	22.0	7.5	15.3	77.2	42.0	5.5	0.1	44.9	0.8	1.6	15.8
WP	58.8	9.4	21.9	5.7	17.2	77.2	53.7	6.7	0.0	33.9	0.5	1.5	17.6
WS	22.0	42.0	30.0	6.5	15.0	78.5	43.1	5.8	0.0	44.6	0.8	1.6	16.7
WSP	23.0	44.0	26.0	0.2	18.0	81.8	48.0	6.2	1.8	43.8	0.7	1.5	18.0

*Calculated using Dulong equation (Mason & Gandhi, 1980)

2.3.2 **Experimental set up**

Throughout the thesis all pyrolysis experiments were conducted using the apparatus shown in Figure 2-1. A photographic representation of the small-scale batch pyrolysis unit can be found in Appendix 5 (Figure A5-3).

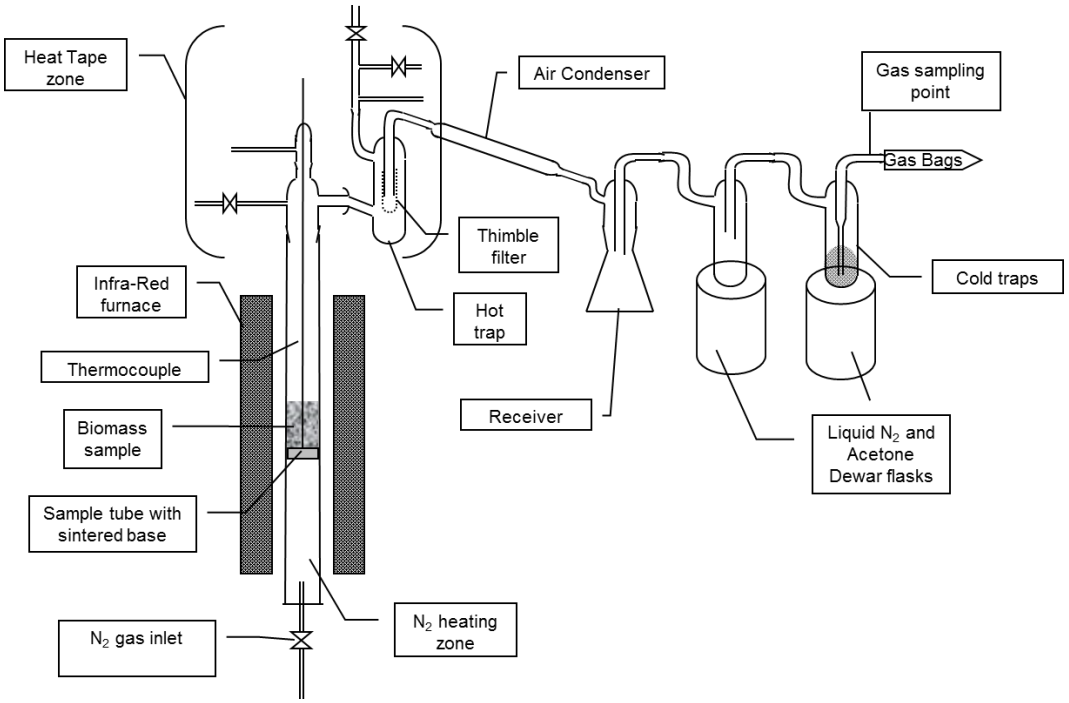

Figure 2-1: Schematic of small-scale laboratory batch pyrolysis unit situated at UKBRC, The University of Edinburgh.

The small-scale batch pyrolysis unit consisted of a fixed bed reactor formed from a vertical 50 mm diameter quartz tube with sintered plate at the base allowing a sample bed depth of up to approximately 200 mm. The sample tube was then placed within a 12 kW infra-red gold image furnace (P610C; ULVAC-RIKO, Yokohama, Japan) with a proportional–integral–derivative controller and a remote computer control, allowing for the application of a wide range of heating rates and hold times at an array of maximum HTTs. Monitoring and control of temperature in the sample bed was carried out using a thermocouple positioned 10 mm from the inner surface of the quartz tube to allow for a reasonable response to applied heat from the furnace. Prior to pyrolysis the system was purged via the bottom of the pyrolysis tube with N_2 to

remove any external sources of air before establishing a steady flow rate (0.33 $\pm$ 0.02 L min^{-1}) to sweep volatiles and gas through a condensation system. This condensation system, as seen in Figure 2-1, consisted of two regions of cooling to remove condensable volatiles from the gas phase. The first section (heat tape zone) was continuously heated (160 $\pm$ 10^{o}C) and used to remove entrained particulates on a thimble filter while collecting high-boiling tars in a separate trap (hot trap). The second section consisted of a series of condensers and receivers to collect liquid products, firstly at room temperature (Receiver) and secondly at < -35^{o}C (cold traps).

At the end of the condensation system non-condensable pyrolysis gas was collected in a 200 L multi-layered gas bag (Jensen Inert Products, Coral Springs, Florida). When the end of the residence time was reached the sample was gradually cooled (with continued N_2 flow) until below 100^{o}C (about 1 hour) and removed for storage. Data for the main process variables such as temperature, pressure and gas volume flow were logged in real time.

2.3.3 **Product collection**

After pyrolysis, product masses were determined for char and condensed liquids by gravimetric (2 d.p.) difference of equipment before and after experiments. The mass of the gas fraction was calculated using the product gas volume, measured using a volumetric flow meter (TG5 Gas meter, Ritter, Germany) and gas composition analysed using a quadrupole mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK) (Figure A5-5). Yields of each product (gas, liquid and char) were calculated as a proportion of feedstock weight on a dry weight basis. The char product was removed from the pyrolysis tube and retained for analysis while the condensed liquid products comprising heavy tar, lighter oil fractions and water were collected in separate vials (as shown in Figure A5-6) and stored in a freezer to slow-down liquid aging.

2.4 Sample Analysis

Once produced, biochar samples were then analysed by several established methods to determine composition and energy properties, as well as by new techniques developed at UKBRC for determining biochar functional properties. Liquid and gas co-products were analysed for various properties when appropriate to the overall objectives of the PhD, but not consistently for every sample. The following section describes the analytical procedures performed throughout the PhD project.

2.4.1 Physicochemical properties

2.4.1.1 Proximate analysis

Proximate analysis has long been established for assessing the quality of coal and charcoal fuels through quantifying the concentrations of moisture, 'volatile matter', 'fixed C' and ash. Prior to proximate analysis biochar samples were crushed to a homogenous fine powder using a ball mill (MM200; Retsch, Castleford, UK) and dried overnight at 105^{o}C. The analysis of all biochar samples and corresponding feedstock, unless stated otherwise (section 3.2.4), was carried out using thermal gravimetric analysis (TGA) (TGA/DSC 1; Mettler-Toledo, Leicester, UK) at UKBRC. Due to the small amount needed (mg) for TGA analysis, moisture can be rapidly absorbed by the sample during transport and handling prior to analysis. Samples were first heated for 10 min at 105^{o}C under N_2 to determine moisture content; the temperature was then raised at 25^{o}C min^{-1} to 900^{o}C where it remained for a further 10 min to determine volatile matter content. Finally, air was introduced to the system combusting the sample (also at 900^{o}C) for 20 minutes in order to determine the ash content. Fixed C was then calculated on a weight percent basis by subtracting moisture, volatile matter and ash values from the original starting mass. The high temperatures applied during proximate analysis have been shown to cause volatilisation of particular ash minerals (P, K, Mg etc.) (Darvell *et al.*, 2005; Okuno *et al.*, 2005; Enders & Lehmann, 2012; Enders *et al.*, 2012). However, high temperatures are required to ensure the complete decomposition of recalcitrant pyrolytic materials (Enders *et al.*, 2012).

2.4.1.2 Ultimate analysis

Elemental (ultimate) analysis is the determination of C, hydrogen (H), nitrogen (N) and other major components (e.g. sulphur) via the analysis of the gaseous product following complete combustion. Analysis was conducted in duplicate using an elemental analyser (Flash 2000, CE Elantech Inc., New Jersey, USA) by London Metropolitan University (London, UK). The oxygen (O) concentration was determined by the subtraction of ash content and measured elemental components from 100%.

2.4.2 Biochar functional properties

2.4.2.1 Edinburgh toolkit

The effect of process conditions on the physical and chemical properties of biochar has been extensively covered throughout literature, however investigations into the functional properties of biochar are currently under researched. In order for the full C sequestration and agronomical potential of biochar to be realised, the impact of biochar following its application to the environment needs to be thoroughly assessed prior to deployment. The importance of such an analytical tool led Dr Andrew Cross and Dr Saran Sohi at the UKBRC, Edinburgh to develop a biochar screening tool kit. The Edinburgh tool kit is a set of analytical techniques utilised to screen biochar samples for 5 key functional attributes:

- Stable-C (Cross & Sohi, 2013)
- Labile-C (Cross & Sohi, 2011)
- SOM priming (Cross & Sohi, 2011)
- Nutrient value
- Soil structural impacts

Due to the large sample requirements for some of the analytical tools in conjunction with low char yields obtained from pyrolysis experiments as well as time and analytical cost constraints, only stable-C and labile-C tools were used to analyse the biochar samples produced during this PhD. The stable-C and labile-C analytical procedures are therefore briefly described in the following sections.

2.4.2.1.1 **Stable-C Tool**

Biochar samples were treated by direct chemical oxidation in an attempt to simulate the environmental ageing of biochar, through mimicking enzymatic soil processes, to provide a measure of biochar C stability (stable-C %). Physical macrostructures can potentially protect biochar from oxidation through limiting the full exposure of biochar's surface area to chemical oxidation. Therefore this potential protection was removed prior to treatment by milling all biochar samples to a fine powder in a ball mill (Retsch MM200, Retsch, Castleford, UK). Samples were dried overnight at 80^{o}C to remove moisture and stored in a desiccator. Prior to treatment, the total C concentration of each biochar sample was determined through ultimate analysis (see section 2.4.1.2). The total C was then used to weigh out (4 d.p.) an amount of each biochar sample equivalent to 0.1 gC into a glass test tube. The samples were then treated with 0.01 mol of hydrogen peroxide (H_2O_2) (certified analytical reagent, Fischer Scientific, Loughborough, UK) in a solution of 7 ml deionized water, while agitating the test tube to ensure all biochar was in suspension (Cross & Sohi, 2013). Tubes were then heated (80^{o}C) for 2 days to introduce a thermal oxidation step. During this step the test tubes were agitated 2-3 times per day. Following the 2 days of heating, the samples were dried in an oven at 105^{o}C overnight. Mass loss was then determined by reweighing the tubes following a cooling period in a desiccator. Analysis was performed in triplicate for each sample. Total C determination was further performed on a combined post ageing residue and used in conjunction with the measured mass loss for each replicate to express the stability of biochar C as a proportion of initial C remaining after chemical oxidation (Cross & Sohi, 2013). While the stable-C tool uses chemical oxidation to mimic the oxidative degradation of biochar caused by peroxidase enzymes, this technique cannot completely replicate environmental processes. By focusing on the oxidation of biochar the process does not account for the degradation of biochar through hydrolysis steps which are likely to occur within the environment. Furthermore, biochar samples were milled prior to oxidation as a means of removing any physical protection to the oxidation process, which could potentially lead to an underestimation of the environmental stability of biochar. Stability could also be further underestimated by failure to account for the

potential stabilisation of biochar with soil minerals. Photographic representation of the stable-C tool can be found in Appendix 5 (Figure A5-7).

2.4.2.1.2 **Labile-C tool**

The labile-C tool was developed to assess the short term impact of biochar application on the native carbon stock. This small short term flux of labile-C from biochar had previously been measured (Zimmerman, 2010; Bruun *et al.*, 2011) and could cause the mineralisation of SOM, ultimately affecting the overall C sequestration potential of biochar. Short term incubations were therefore used to measure the proportion of labile-C present in biochar samples. Biochar (2.0 g) was crushed and added to sterilised size-graded quartz sand (19.0 g) which was then inoculated with micronutrient solution and soil microbes. The water holding capacity of the mixture was then adjusted to 65 % and placed into an incubator at 30^{o}C for two weeks. The evolution of CO_2 in each flask as a result of carbon mineralisation was determined gravimetrically by soda lime adsorption through proportional weight increase of the soda lime (Cross & Sohi, 2011). Each biochar set consisted of 4 replicates and one control blank to correct for the CO_2 gained during preparation of the vials, the flask headspace and re-drying of soda lime prior to weighing. The proportion of mineralised C was then established through use of a conversion factor and expressed as a percentage of the total C (Cross & Sohi, 2011). The incubation of biochar was performed using a sand medium as opposed to soil, so that the measurement of labile-C was not compounded by soil mineralisation. While this allowed for measuring the labile-C content of biochar it also fails to include soil specific differences which could be faced in the environment. Photographic representation of the labile-C incubations can be found in Appendix 5 (Figure A5-8).

2.4.2.2 **pH**

Measurements of biochar pH values were carried out following the procedure described by Rajkovich *et al.* (2011) identified as a suitable technique by the International Biochar Initiative (IBI, 2013). Biochar pH values were obtained using a ratio of 1.0 g of biochar in 20 ml of deionized water. Before pH measurements were taken the samples were shaken (Orbital Multi-Platform Shaker PSU-20i, Grant

instruments Ltd, Shepreth, Cambridgeshire, UK) for 1.5 hours to ensure sufficient equilibration between biochar surfaces and solution. The pH measurements were taken using a bench top pH probe (Mettler-Toledo FE20, Mettler-Toledo, Columbus, OH, USA) and performed in triplicate.

2.4.2.3 Nutrient extraction analysis

Biochar samples were analysed to determine the concentration of extractable Ca, K, Mg, Na, P and CEC. A full description of the analytical procedure for determining the extractable bases and CEC can be found in Appendix 4.

2.4.2.4 CEC and extractable nutrients

Biochar CEC was assessed using the ammonium acetate method (Faithfull, 1985) where ammonium was extracted from biochar with acidified potassium chloride and quantified colorimetrically. The concentrations of extractable ions were determined by dry ashing, dissolving in hydrochloric acid and analysing by ion chromatography.

2.4.2.4.1 Total and extractable phosphorus

Biochar total phosphorus content was determined by ashing at 550^{o}C for 4 hours followed by aqua regia digestion (highly corrosive mixture of nitric acid and hydrochloric acid optimally in a volume ratio of 1:3) under heating (BS EN 13650, 2001). The remaining residue was then analysed using inductively coupled plasma – optical emission spectrometry (ICP-OES). Extractable P was estimated using the Olsen P method (Olsen *et al.*, 1954; BS7755-3.6, 1995).

2.4.3 Energy content of pyrolysis co-products

The higher heating value (HHV) is the heat energy released when a compound is completely combusted under standard conditions. To investigate the influence of process conditions on the distribution of energy between the co-products of slow pyrolysis and determine the total energy balance, the HHV for biochar, liquid and gas products were calculated. The following section briefly explains the analysis steps for each product.

2.4.3.1 Biochar HHV

Biochar samples were analysed for HHV using an adiabatic bomb Calorimeter PAR 1261 (accuracy of $\pm$ 0.1 % (n = 2)) at Pemberton Analytical Services (Shawbury, Shropshire, UK). A homogenous dry sample of between 0.5 g and 1.0 g was weighed out into a crucible and mounted in the bomb head which was then assembled and charged with oxygen. The bomb chamber (stainless steel) in which the combustion takes place was submerged in a bucket filled with a known volume of water (2 L) at a known temperature ($30^{o}C \pm 1^{o}C$). The water was continuously stirred and the ambient temperature recorded before combustion as well as the maximum temperature rise after combustion. The bucket containing the bomb camber was placed in the calorimeter and the calorimeter turned on. The change in water temperature is then used to calculate the calorific value of the sample in MJ $kg^{-1.}$ Analysis was performed in duplicate to provide statistical variation.

2.4.3.2 Liquid HHV

Liquid samples are separated from the gas stream through a series of condensation traps as shown in Figure 2-1. This led to the collection of three different liquid fractions consisting of heavy tars, light liquids condensed at room temperature and finally liquids collected from the first cold trap. Sub samples of these three fractions were then added together to create one representative liquid sample for calorific analysis. The calorific analysis of liquid samples was carried out at the University of York using an isoperibol oxygen bomb calorimeter, model Parr 6200. The liquids were treated with a known amount of solvent (dodecane) to dissolve the different fractions into one homogenous state while also overcoming the difficulty of igniting liquids with high moisture contents. The energy value of the solvent (44.15 kJ g^{-1}) was then subtracted from the total energy value to determine the HHV for the pyrolysis liquid fraction. Duplicate samples were prepared to test the variation in the analysis procedure.

2.4.3.3 Gas analysis

Gas samples were collected during each pyrolysis experiment using 200 L multilayer gas bags, as described in section 2.3.2. The gas bags were then left to rest for 30

minutes to allow the mixture to equilibrate, after which the overall composition of the collected gas sample was analysed for N_2, H_2, CO, CO_2, CH_4, C_2 hydrocarbons , O_2 and argon (Ar) on a volume basis, using a quadrupole mass spectrometer (HPR-20 QIC, Hiden Analytical, Warrington, UK). As both CO and N_2 give parent peaks at mass 28 it was difficult to differentiate between them, particularly as other species being analysed also have peaks present at mass 28. To solve this problem pure N_2 was sampled and the ratio of N_2 at mass 14 and 29 was determined which then allowed for the calculation of N_2 at mass 29 by measuring N_2 at mass 14 during the experiments. Once the amount of N_2 at mass 29 was determined it was subtracted from the remaining measurements at mass 29 leaving only CO at mass 29. The mass spectrometer could not distinguish between C_2 hydrocarbons so for the sake of mass and HHV calculations the C_2 hydrocarbon fraction was assumed to be and therefore further referred to as ethane (C_2H_6). The final composition of the pyrolysis gas was corrected for the dilution effect of the carrier gas (N_2) but the heating values of pyrolysis gas were still calculated with N_2 concentration taken into account. This was to allow for a direct indication of the energy contained in the gas stream of the pyrolysis system without any upgrading processes. The results of gas HHV/lower heating value (LHV) and cold gas efficiency (CGE) were calculated by the following equations:

$$m_{\text{gas}}\,[kg] = m_{\text{H2}} + m_{\text{CO}} + m_{\text{CH4}} + m_{\text{C2H6}} + m_{\text{CO2}}$$

$$HHV_{\text{gas}}\,[\text{MJ/kg}] = \left((m_{\text{H2}} \times HHV_{\text{H2}}) + (m_{\text{CO}} \times HHV_{\text{CO}}) + (m_{\text{CH4}} \times HHV_{\text{CH4}}) + (m_{\text{C2H6}} \times HHV_{\text{C2H6}})\right) / \text{m}_{\text{gas}}$$

The LHV of the product gas was then determined through subtracting the latent heat of vaporisation of water. To compare the efficiency of converting biomass using different technologies and under different conditions, the CGE is often used. The CGE can be determined as:

$$CGE\,[\%] = \left((LHV_{\text{gas}} \times m_{\text{gas}}) \,/\, (LHV_{\text{feed}} \times m_{\text{feed}})\right) \times 100$$

2.4.4 **Statistical analysis**

The chapters presented within this thesis were produced by three separate "fully crossed design" experiments where the influence of production conditions was investigated (Box *et al.*, 2005). Using this type of experimental design meant that each combination of experimental conditions was only performed once. This design was possible as preliminary tests showed very good reproducibility of experimental conditions (Table 2-3). The monitoring of the pyrolysis process was such that any discrepancies in the process conditions would be detected and the run and results discarded.

Table 2-3: Three pyrolysis experiments repeated under the same conditions to determine reproducibility of system

Feedstock	Peak temperature [^{o}C]	Time at Peak Temp [min]	Heating rate to Peak Temp [^{o}C/min]	Heating rate overall [^{o}C/min]	Char Yield [wt.%, (db)]
Willow wood chips	650.4	18.3	71.2	32.5	20.7
Willow wood chips	650.3	18.2	71.8	32.6	21.2
Willow wood chips	650.1	18.1	71.9	32.3	21.0
Standard Deviation	0.15	0.10	0.36	0.15	0.25

It was important to demonstrate the relevance of our analytical results and whether the trends observed were statistically significant or not. Therefore analysis of variance (ANOVA) statistical test was applied through a general linear model using Minitab 16 statistical software and significance of results were calculated at a significance level of $P < 0.05$ for all materials and production conditions. Correlations were performed using Spearman rank method and R values were categorised by considering correlation coefficients ≤ 0.35 to represent low or weak correlations, 0.36 to 0.67 to be moderate correlations, 0.68 to 0.89 strong or high correlations and ≥ 0.9 to be a very high correlation (Taylor, 1990). Chapter 7 focuses on the statistical analysis of the entire data set collected within this thesis and uses linear regression equations produced by Minitab 16 software to estimate biochar properties.

2.5 Experimental limitations

The experimental plan in section 2.3.1 was designed to investigate the combined influence of several process conditions (HTT, heating rate, residence time, carrier gas flow rate) and a variety of feedstock types (Table 2-1). As reported in Chapters 3, 4, 5 and Appendix 2, this design lead to the production of 83 biochar samples, rising to > 100 pyrolysis experiments when repeated runs and additional feedstock types, not considered for the main results of the thesis, were included. The number of production conditions investigated throughout this thesis and the extent of analytical testing on biochar samples was limited mainly by time, financial constraints and availability of both starting material and final biochar product. Investigating a larger number of process parameters would have diminished the level of investigation possible and vice versa. Laboratory time was also spent developing the operational design of the pyrolysis system, incorporating a mass spectrometry for on-line gas analysis and training of other UKBRC personnel on the pyrolysis unit and mass spectrometer. High demand for the pyrolysis unit as well as regular maintenance (carried out by the candidate) of the pyrolysis unit and mass spectrometer also limited the extent of biochar production for the thesis. If more time was available then further studies on additional production conditions would have been considered, as well as extra functional properties to expand the systematic set of biochar samples and the size of data set for determining statistical relationships.

Chapter 3. **Determining the influence of production conditions on the environmental stability of biochar**

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The candidate, as lead author, was solely responsible for all experimentation, laboratory analysis (unless stated otherwise), data analysis and writing of the paper. Co-authors provided guidance and support on the scope and design of the project, the analyses performed and contributed to the editing of the manuscript. Andrew Cross also provided assistance during laboratory analysis while Peter Brownsort was instrumental in the initial set up of the pyrolysis system.

Figure 3-2, Figure 3-3 and Figure A1-1 have been amended from the version published to express the yields of stable-C, fixed C, volatile matter and total C on a feedstock C % basis rather than the original feedstock weight basis. This allowed for a better understanding of the effect on overall C stability and so improved the investigation of Objective 1.

Abstract

In general, most biochar can be considered resistant to chemical and biological decomposition, and therefore suitable for C sequestration. However, to assess the C sequestration potential of different types of biochar, a reliable determination of their stability is needed. Several techniques for assessing biochar stability have been proposed, e.g. proximate analysis, O:C ratio and H:C ratio, however, none of them are yet widely recognised nor validated for this purpose. Biochar produced from three types of feedstock (PC, RH and WS) at four HTTs (350^{o}C, 450^{o}C, 550^{o}C and 650^{o}C) and two heating rates (5^{o}C min^{-1} and 100^{o}C min^{-1}) was analysed using three methods of stability determination: proximate analysis, ultimate analysis and direct oxidation (stable-C tool). As expected, increased pyrolysis HTT resulted in higher fractions of stable-C and total C due to an increased release of volatiles. Data from the direct oxidation of biochar was compared with that obtained by the other methods, i.e. fixed C, volatile matter, O:C and H:C ratio, to investigate potential relationships between them. Results of this comparison showed that there was a strong correlation ($R > 0.79$) between the stable-C determined by direct oxidation and fixed C, volatile matter and O:C, however H:C showed a weaker correlation ($R = 0.65$). An understanding of the influence of feedstock and production conditions on the long term stability of biochar is pivotal for its function as a C mitigation measure, as production and use of unstable biochar would result in a relatively rapid return of C into the atmosphere, thus potentially intensifying climate change rather than alleviating it.

3.1 Introduction

Biochar is the C-rich solid produced by thermo-chemical conversion (pyrolysis) of biomass in an oxygen depleted environment for the purpose of soil amendment. Biomass pyrolysis diverts C away from the dynamic atmosphere–biosphere pool and into a far more stable pool decomposing at a much slower rate than its parent feedstock (Preston & Schmidt, 2006; Liang *et al.*, 2008; Spokas, 2010) avoiding the complete return to the air of CO_2 from natural decay or burning. Producing biochar and incorporating it into soil for the purpose of soil improvement is thus one proposed method to increase long term storage of C in the biosphere (Shackley & Sohi, 2010; Sohi *et al.*, 2010). As a relatively complex proposition that concerns energy production as well as C sequestration and soil management, it is the subject of increasing multi-disciplinary research. It is known that the physiochemical properties of biochar depend on the starting organic material, the carbonization system used to make it and selected production parameters (Enders *et al.*, 2012).These properties then define the functional properties such as biochar soil stability which is essential to demonstrate the longevity of stored C and therefore establish an effective means for C abatement.

Biochar can be considered part of the black C continuum, a term used to describe the by-products of combustion that also includes – in order of increasing stability – charcoal, coal, soot and graphite (Baldock & Smernik, 2002; Masiello, 2004; Liang *et al.*, 2008). Through the use of C-14 dating, black C has been found to be the oldest fraction of C in soils, with the most stable components displaying MRTs of several thousand years (Preston & Schmidt, 2006; Liang *et al.*, 2008; Lehmann *et al.*, 2009). The complexity and chemical heterogeneity of black C has made it difficult to establish a single method suited to assessing the potential stability of all materials in the continuum (Hammes *et al.*, 2006) and hence, there is no globally-established method for determination of absolute stability for black C or biochar. However, a number of methods for comparing the relative stability of different biochar materials have emerged. These include proximate analysis (ASTM D1762-84, 1990; Antal &

Grønli, 2003), O:C or H:C molar ratios (Spokas, 2010; Enders *et al.*, 2012; IBI, 2013), and chemical oxidation (Cross & Sohi, 2013).

Proximate analysis has long been used to assess the quality of coal and charcoal fuels, defining moisture, "volatile matter", "fixed C" and ash. Proximate analysis requires high temperatures (900^{o}C for determination of volatile matter and 750^{o}C for ash determination) for extended periods of time. This has practical drawbacks and can lead to an inflated estimate of fixed C by underestimation of ash content (Masiello, 2004; Downie *et al.*, 2009; Enders *et al.*, 2012). Furthermore, proximate analysis relies on thermal decomposition for calculation of products, which does not provide an analogue for the degradative (primarily oxidative) processes that exist in soil.

Pyrolysis favours the elimination of H and O over C, such that extending pyrolysis reactions result in a solid residue (char) of progressively higher C concentration. The utility of elemental ratios, provided by ultimate analysis, as indicators of biochar stability has been extensively researched (Kuhlbusch, 1995; Hedges *et al.*, 2000; Masiello, 2004; Spokas, 2010; Schmidt *et al.*, 2012). The O:C ratios assigned to materials encompassed by the black C continuum showed a systematic increase from 0 for graphite to > 0.6 for material not considered to be black C. For aged biochar samples, changes in O:C ratio at the surface indicates the extent to which they have been oxidised by their environment (Cheng *et al.*, 2006). For newly produced samples, O:C indicates the progression of deoxygenation which can serve as a proxy for the extent of charring. Correlation of O:C with the MRT of various biochar samples in soil, extrapolated from various short-term incubation experiments confirmed a general, inverse relationship between this ratio and biochar stability (Spokas, 2010). This work proposed that biochar displaying an O:C ratio > 0.6 would be closer to biomass composition than to graphite and would have a MRT < 100 years. Conversely, material with an O:C ratio in the range 0.2 – 0.6 would be expected to have a MRT of 100 – 1000 years. To avoid confounding analyses with non-black C species, IBI guidelines for quantifying O:C ratio recommend the

application of an acid treatment for the removal of carbonates and determination of organic C (IBI, 2013).

The ratio of H:C has also been proposed as an index of aromaticity and resistance of char to microbial and chemical degradation (Kuhlbusch, 1995; Kuhlbusch & Crutzen, 1995). As with O:C quantification, pre-treatment steps (acid and thermal treatment) can be applied to remove inorganic and organic C prior to total H and C determination. Kuhlbusch (1995) also described the use of a correction factor to exclude H bound to elements other than C, most likely silicate, therefore generating an H:C ratio only for the stable fraction of char. However, Enders *et al.* (2012) showed that their results ranked poultry manure, based on H:C ratio, to have equal stability to woody samples which were found to be much more stable thus creating doubt over the suitability of H:C as a method of determining stability.

In order for the potential of biochar for C sequestration and agricultural benefit to be fully realised, it is necessary that the different functional characteristics of biochar such as stability can be rapidly assessed prior to deployment. The method put forward by Cross & Sohi (2013) establishes an approach that directly quantifies stability by eliminating the less stable portion of material by oxidation. Controlled but fast addition of H_2O_2 is used as an analogue for the accumulated effect of oxidation over extended periods of time in soil. Biochar samples produced under subtly different conditions can be readily distinguished and the oxidation treatment tuned to mimic the loss of C occurring in charcoal over 50 – 200 years in the environment (depending on ambient climate conditions). This approach has the potential to capture the effects of the physical inaccessibility of biochar as a substrate, whereas thermal degradation may not. Therefore a comprehensive comparison of the methods described is required for two reasons. Firstly, if methods are equivalent or can be correlated, the more practical and cost effective method may be promoted for future applications. Secondly, if results provided by different methods diverge, new insights into the nature of biochar may emerge, for example, the effect of contrasting abiotic conditions in the natural environment.

This study investigates the impact that process conditions have on the C sequestration potential of biochar, contributing towards Objective 1 listed in Chapter 1. A systematic set of biochar samples was produced and assessed for C stability using proximate analysis, elemental molar ratios and direct oxidation. The aim of using three techniques was to determine whether the different assessment methods provided a measure of the same characteristics and, where results showed different patterns, to consider the possible reasons. Comparisons between stability on a biochar C basis and a feedstock C basis were used to investigate the overall C sequestration potential of biochar and the impact that varying production conditions may have on this potential (Objectives 1 and 3).

3.2 Materials and methods

3.2.1 Feedstock

The three types of biomass used for the pyrolysis experiments within this chapter were: pine wood chips (PC), rice husk (RH) and raw wheat straw (WS). The full details of feedstock particle size, moisture content and supplier can be in Table 2-1 in section 2.3.1. Results from ultimate and proximate analysis of the selected materials are also located in section 2.3.1 in Table 2-2. For PC and WS the natural heterogeneity within bulk supply was minimised as far as possible by thoroughly mixing a volume sufficient for all experiments.

3.2.2 Pyrolysis equipment

The experimental set up of the pyrolysis equipment was described in section 2.3.1 and shown in Figure 2-1.

3.2.3 Pyrolysis conditions

Each pyrolysis experiment used a standard volume of feedstock, resulting in a different mass of material being used in runs for different feeds: 40 g for PC, 30 g for RH or 15 g for WS. Each type of feedstock was exposed to HTTs of 350^{o}C, 450^{o}C, 550^{o}C and 650^{o}C using one standard carrier gas flow rate (0.33 $\pm$ 0.02 L min^{-1}) of nitrogen (N_2) and holding time at HTT of 20 min. Samples from all feedstock types were heated at a rate of 5^{o}C min^{-1} while 100^{o}C min^{-1} was also used for PC and RH experiments.

3.2.4 Product analysis

Detailed descriptions of the analytical procedures carried out during this work can be found in section 2.4. In brief, char samples were analysed by proximate analysis, ultimate analysis and direct oxidation. Proximate analysis was carried out using TGA (TGA/DSC 1; Mettler-Toledo, Leicester, UK) at the University of Leeds. Analysis followed the same methodology applied by UKBRC in section 2.4.1.1.

3.3 Results and discussion

3.3.1 Product yield distributions

The yields of char, liquid and gas obtained from each pyrolysis experiment are shown in Figure 3-1. For each feedstock, a higher HTT resulted in a lower char yield, as expected (Antal & Grønli, 2003).The distribution of product char, liquid and gas was heavily dependent on the original composition of biomass prior to pyrolysis. The cellulose, hemicellulose and lignin fractions can vary greatly between feedstock materials and these differences potentially result in contrasting product yields from pyrolysis and also the properties of those products (Vassilev *et al.*, 2010). The lower biochar yields given at higher HTT are a result of greater decomposition of organic material with increasing temperature promoting the release of volatile matter. Differences in volatile matter yields over the temperature range investigated can be a result of the degree of breakdown of cellulose, hemicellulose and lignin (Demirbas, 2004; Mohan *et al.*, 2006; Enders *et al.*, 2012). RH samples yielded the largest mass of char, but conserved mass included high concentrations of inorganics present in the feedstock known from literature to be high in silica (Kalapathy *et al.*, 2000). Increased char devolatilisation at higher temperature then results in a higher percentage of liquid and gaseous products (Figure 3-1). In addition to biochar properties the distribution of the pyrolysis products should be considered when selecting production conditions, since their quality and quantity will determine their end use and so the overall impact of the system (Shackley *et al.*, 2011). For example the changing process conditions had a clear impact on the yields of co-products which could affect the energy distribution between the char, liquid and gas products (investigated further in Chapter 5).

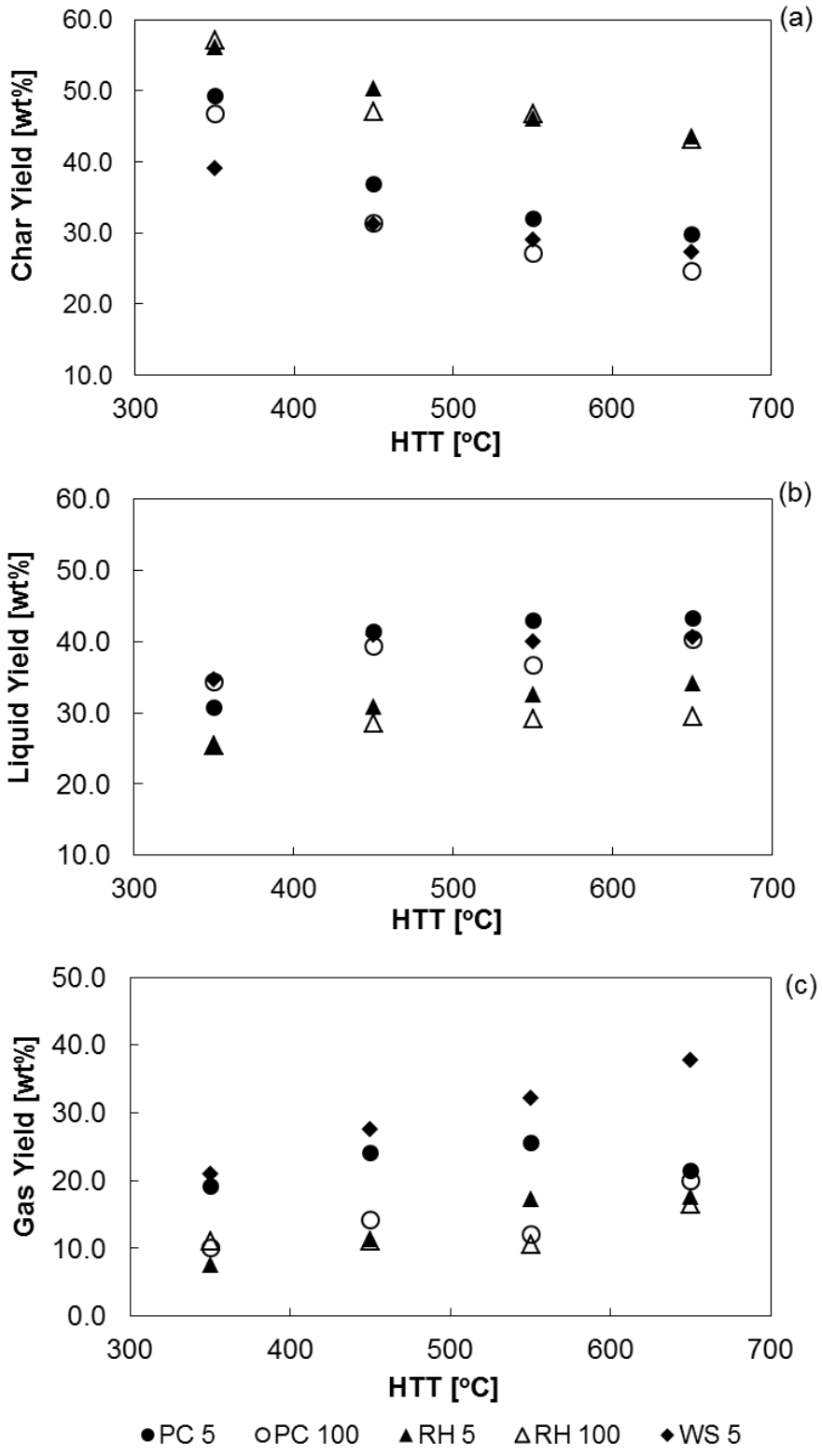

Figure 3-1: Effect of production temperature on the product distribution yield for (a) char (b) liquid (c) gas present on a dry feedstock weight basis.

3.3.2 **Direct oxidation**

Stable-C content (biochar C %), determined by the direct oxidation method (Cross & Sohi, 2013), increased with pyrolysis temperature, for each feedstock (Figure 3-2). Biochar produced from WS contained the highest concentration of stable-C at temperatures < 650^{o}C however analysis of WS biochar produced > 650^{o}C exhibited a decrease in stable-C. The higher stable-C concentration at 550^{o}C could be attributed to the heterogeneous nature of the material used for that experiment resulting in an increased proportion of stable-C present in the feedstock. Expressing results on a feedstock C basis (stable-C yield) removes the direct effect of (conserved) feedstock ash content, although ash may still have influenced the product yields and biochar stability indirectly during the pyrolysis process (Figure 3-2). This measure provides an index for the efficiency of conversion of feedstock C to stable-C, rather than simply how much of the C in a particular biochar is stable.

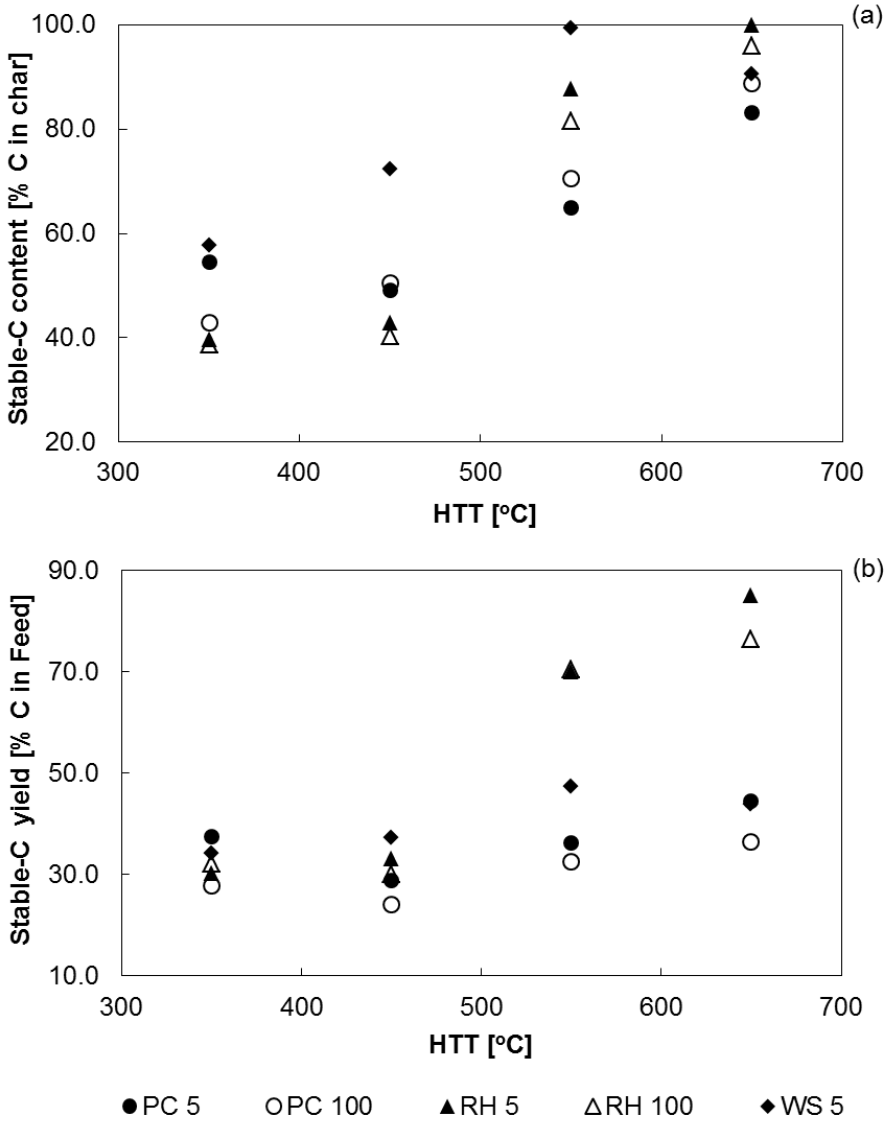

Figure 3-2: Effect of increasing production temperature on the (a) stable-C content and (b) stable-C yield of biochar samples. Figure (b) has been amended from the published version to express stable-C yield on a feedstock C % rather than feedstock wt. % basis. Error bars were added to the graph to show standard error of stable-C % but are not visible due to the scale of the data (n=3).

In contrast to the yield of biochar from pyrolysis, there was a slight increase for stable-C yield of PC and WS biochar in the pyrolysis HTT range of 350°C – 650°C. Despite this small variation for WS (34.2 – 47.4 %) and PC (37.4 – 44.5 %) derived biochar, the stable-C yield for RH samples increased from 33.2 – 70 % when

pyrolysis occurred at HTT above 450^{o}C. This observation could be a result of the high ash content typical for RH.

Heating rate, across the range investigated (5^{o}C min^{-1} to 100^{o}C min^{-1}), did not seem to have a notable impact on stable-C concentration of biochar, although a trend showing slightly lower stable-C yields in samples created at high heating rate could be discerned. A rise in the yield of stable-C with increasing pyrolysis temperature is of particular importance to the economic and environmental case for biochar production. Establishing how pyrolysis–biochar systems can be refined to produce a product that best enhances soil fertility and sequesters C, while also providing energy capture, has been a key question. If the yield of stable-C remains largely unaffected or increases with climbing temperatures then biochar production could be tuned to maximise energy output (see Chapter 5) as well as other important functional properties (see chapter 4) while maintaining the C sequestration potential. The utility of high temperature biochar for soil fertility must then be considered.

3.3.3 **Proximate analysis**

Results of proximate analysis are presented in Table 3-1. The ash concentration of biochar samples was influenced mainly by feedstock ($P < 0.0001$) and to a lesser extent by HTT ($P = 0.003$) with ash content increasing for WS and RH biochar (up to 20 % and 50 % respectively) as HTT was increased but not for PC biochar (<5 %). In contrast to ash, fixed C and volatile matter on a dry ash free basis depended greatly on temperature ($P < 0.0001$) with no influence from feedstock ($P = 0.11$). When ash content was taken into account, however, feedstock had a significant effect ($P < 0.0001$). A strong negative correlation between ash and fixed C ($R^2 = -0.808$, $P < 0.0001$) can be used to reflect why all biochar samples produced from low ash PC contained high levels of fixed C whereas high ash RH biochar exhibited low volatiles and fixed C concentrations. The effect of ash on fixed C content produces a possible limitation of using proximate analysis for the determination of a stable fraction. This is due to the decreasing measured weight of ash leading to inflated values for fixed C determined via subtraction. The loss in weight associated with ash content can be due to volatilisation of ash species such as P, K, Mg, arsenic and selenium during thermal

treatment leading to problems of fouling, corrosion and slagging (Darvell *et al.*, 2005; Okuno *et al.*, 2005; Sonoyama *et al.*, 2006; Enders & Lehmann, 2012).

The fixed C content of biochar increased with pyrolysis HTT due to increasing concentrations of volatile matter being released. Samples produced from PC feedstock showed the highest concentration of volatile matter, as well as the largest decrease (from 55.4 % to 14.8 %) as HTT increased from 350^{o}C to 650^{o}C. Expressed on a feedstock C basis the yield of fixed C increased with pyrolysis HTT for the majority of samples (Figure 3-3).

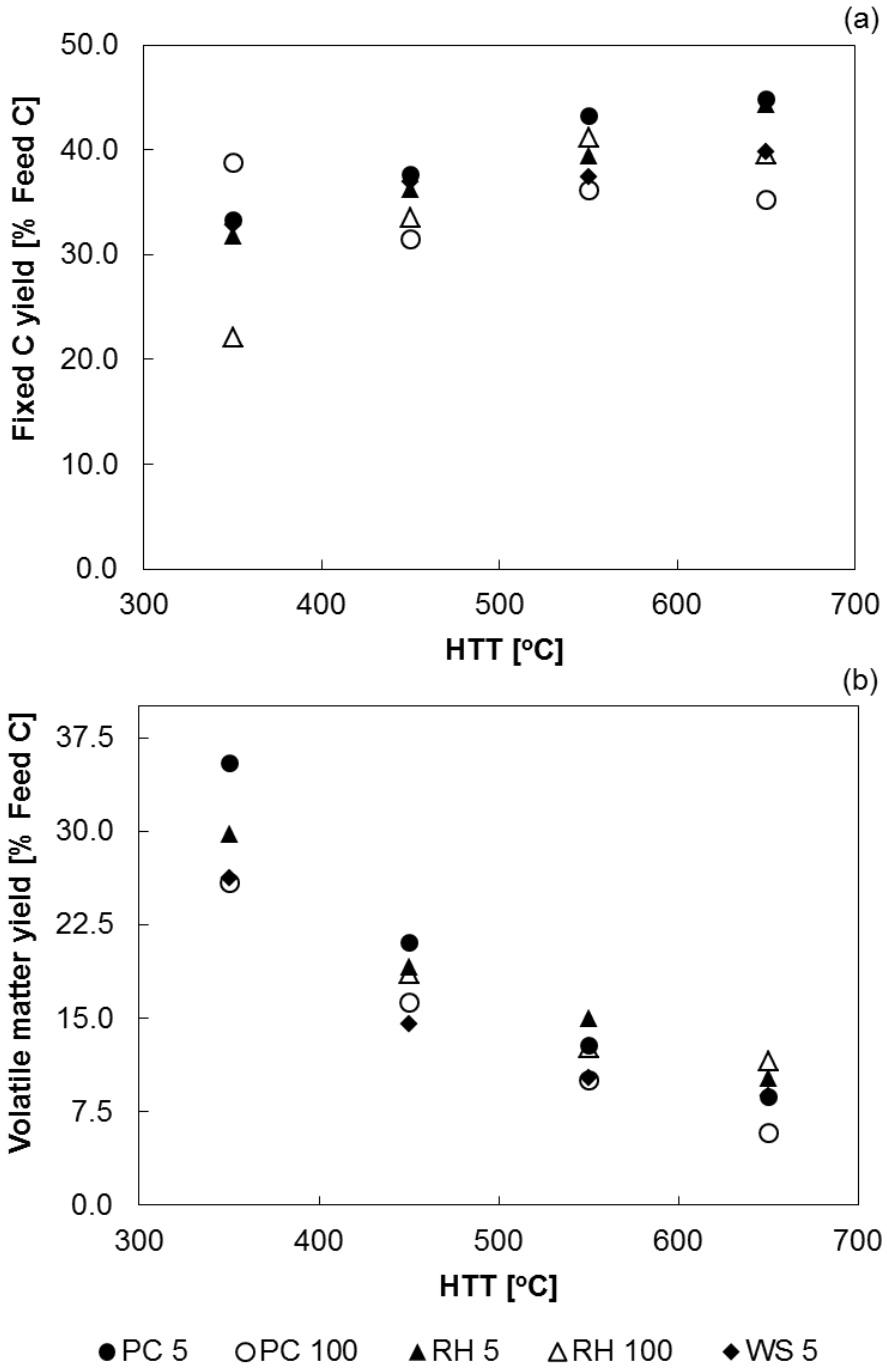

Figure 3-3: Influence of temperature on the (a) fixed C yield and (b) volatile matter yield of biochar samples produced from PC, RH and WS feedstock. Figure (a) and (b) have been amended from the published version to express fixed C yield and volatile matter yield on a feedstock C % basis rather than feedstock wt. % basis.

This confirmed the observations of others (Antal & Grønli, 2003; Mašek *et al.*, 2013a) that overall the yield of fixed C did not change or increased with temperature. This result therefore suggests that certain functional properties enhanced at a higher temperature could be acquired without diminishing C sequestration. As volatile matter follows the reverse pattern to fixed C (Figure 3-3), higher temperature pyrolysis might minimise the biochar fraction susceptible to decay in soil while increasing co-products for heat and power generation (see Chapter 4 and 5). Since small fractions of volatile matter could prove either beneficial (Smith *et al.*, 2010) or detrimental (DeLuca *et al.*, 2009; Jones *et al.*, 2011; Nelissen *et al.*, 2012) to different microbial communities in soil, the composition and ideal amount of volatile matter might need to be researched and quantified. During proximate analysis the biochar sample is exposed to high analytical temperatures which when compared to environment soil conditions can be considered to be extreme therefore minimising the determined stability of carbon. Despite the term, "fixed C" is calculated by weight difference rather than quantification of elemental C and will contain other species of high thermal stability. This combined with the release of volatiles and volatilisation of minerals from the ash phase can lead to an inaccurate determination of C derived from proximate analysis that could be deemed environmentally stable.

Table 3-1: Proximate analysis data (db) for biochar samples produced from selected feedstock at four temperatures (350°C, 450°C, 550°C and 650°C) and two heating rates (5°C min^{-1} and 100°C min^{-1}).

Proximate analysis (db)				
Sample	Fixed C %	Volatile Matter %	Ash %	Total %
PC 350-5	47.8	50.8	1.4	100.0
PC 450-5	62.2	34.9	2.9	100.0
PC 550-5	73.9	22.0	4.2	100.1
PC 650-5	78.9	15.2	5.9	100.0
PC 350-100	58.0	38.7	3.4	100.1
PC 450-100	63.6	33.0	3.4	100.0
PC 550-100	77.7	21.6	0.7	100.0
PC 650-100	81.6	13.4	5.0	100.0
RH 350-5	32.4	30.3	37.3	100.0
RH 450-5	36.4	19.1	44.5	100.0
RH 550-5	38.5	14.6	46.9	100.0
RH 650-5	40.5	9.3	50.3	100.1
RH 350-100	39.3	20.7	40.1	100.1
RH 450-100	35.0	19.4	45.6	100.0
RH 550-100	37.0	11.3	51.7	100.0
RH 650-100	38.6	11.3	50.0	99.9
WS 350-5	49.5	39.6	10.9	100.0
WS 450-5	59.2	23.2	17.6	100.0
WS 550-5	62.8	17.2	20.0	100.0
WS 650-5	64.4	14.2	21.3	99.9

3.3.4 **Ultimate analysis**

Results for all biochar samples are shown in Table 3-2. Statistical analysis indicated that HTT ($P < 0.0001$) was the main determinant of CHNO results expressed on a dry ash free basis (daf). However, similar to proximate analysis, when the ash concentration was included in the CHNO results, the impact of feedstock increased ($P = 0.547$, $P = 0.001$) to become equally important as HTT. For biochar from each feedstock, biochar C content increased with HTT (and inversely to biochar yield) through preferential elimination of N, H and O in volatile matter. Loss of O and H can be attributed to the scission of weaker bonds within the char structure such as alkyl–aryl ether bonds and the formation of more resistant structures (Demirbas, 2004). Total C content for all biochar samples was considerably greater than the total C of their respective biomass. However, when the total C concentration was expressed on a feedstock C basis it was found (Figure A1-1) to decrease with increasing pyrolysis HTT. The effect of elemental composition on the molar ratios O:C and H:C was also assessed in Appendix 1 (Figure A1-2).

Table 3-2: Ultimate analysis of C, H, N and O for all biochar samples and corresponding O:C and H:C ratios on a dry ash free basis (daf).

	Ultimate analysis (daf)					
Sample	C%	H%	N%	O%	O:C	H:C
PC 350-5	69.6	3.8	0.0	26.6	0.29	0.65
PC 450-5	79.9	2.7	0.0	17.5	0.16	0.40
PC 550-5	89.9	1.6	0.0	8.5	0.07	0.21
PC 650-5	94.6	2.0	0.0	3.4	0.03	0.25
PC 350-100	71.0	4.9	1.4	22.7	0.24	0.83
PC 450-100	77.3	3.7	1.0	17.9	0.17	0.57
PC 550-100	82.3	3.0	0.8	13.9	0.13	0.43
PC 650-100	87.9	2.4	1.5	8.3	0.07	0.32
RH 350-5	66.1	4.7	0.0	29.2	0.33	0.84
RH 450-5	74.9	4.1	0.0	21.0	0.21	0.65
RH 550-5	84.0	3.4	0.0	12.5	0.11	0.49
RH 650-5	95.1	2.9	0.0	2.0	0.02	0.36
RH 350-100	70.9	5.4	0.0	23.8	0.25	0.90
RH 450-100	76.9	4.3	0.0	18.9	0.18	0.66
RH 550-100	90.0	3.6	0.0	6.4	0.05	0.48
RH 650-100	89.6	2.7	0.0	7.6	0.06	0.36
WS 350-5	70.9	5.5	1.7	22.0	0.31	0.92
WS 450-5	83.1	5.4	1.4	10.1	0.12	0.77
WS 550-5	86.2	3.6	0.8	9.4	0.11	0.50
WS 650-5	94.9	3.7	1.5	0.0	0.00	0.46

All biochar samples had lower H:C and O:C ratios than their parent biomass owing to preferential elimination of O and H relative to C in volatile matter. Due to the use of molar ratios, small changes in H content had a proportionally larger effect on H:C than the respective changes in O. Both ratios decreased in biochar with increasing pyrolysis HTT. The ratio of H:C at each temperature decreased in the order WS > RH > PC, implying that PC feedstock yielded biochar of the highest stability – an alternative outcome to that obtained from O:C and stable-C analysis. Although for the majority of biochar samples the N concentration was below measurable limits, particular samples showed an increase in N content compared to that measured

within the starting material. This increase could be a result of daily variation in the analytical procedure applied during calibration of equipment and duration of analysis. While the variation in N content could have influence the final H concentration and therefore the H:C ratio the same effect is also likely to influence the O:C ratio to the same extent.

Van Krevelen diagrams plot H:C against O:C to provide clear, visual indication for the origin and maturity of petroleum and coal and more recently applied to biochar to demonstrate the evolution of composition with temperature (Hammes *et al.*, 2006; Preston & Schmidt, 2006). In Figure 3-4, samples from the current work are identified by feedstock and grouped graphically by pyrolysis HTT. Biochar samples residing furthest to the right on the O:C scale were produced at 350°C, with those created at a higher temperature grouped progressively closer to the origin. Results for additional materials in the literature have been added to Figure 3-4, to indicate how the present samples compare to coal and lignite (Hammes *et al.*, 2006; van der Stelt *et al.*, 2011) as well as the regions of stability defined by Spokas (2010) and classification guidelines for biochar (Schmidt *et al.*, 2012; IBI, 2013).

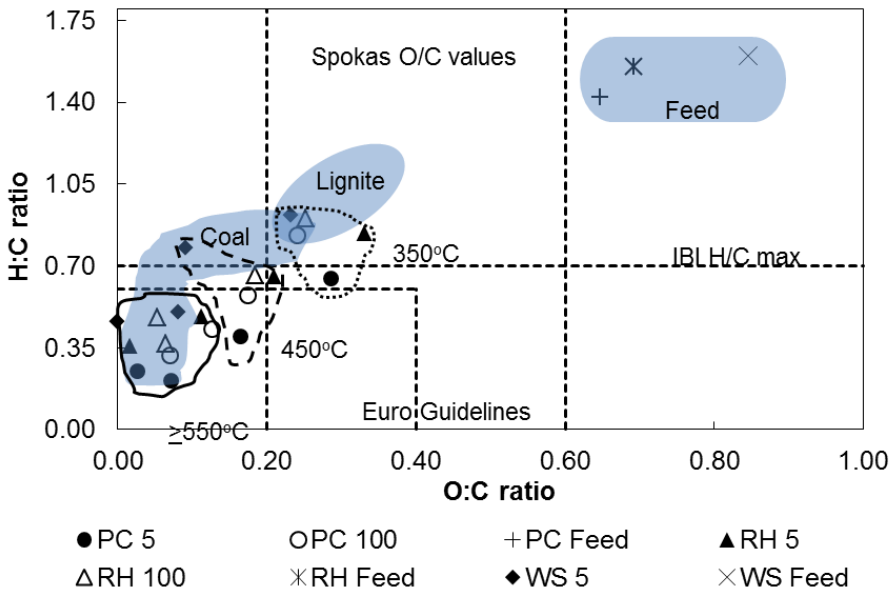

Figure 3-4: Van Krevelen diagram comparing the O:C and H:C ratios of biochar samples with guidelines obtained from literature.

3.3.5 Comparison of stability determination

Individually, five approaches to comparing the stability of biochar suggested increasing biochar stability with higher pyrolysis temperature: increases in stable-C, fixed C content and a decrease in volatile matter, O:C and H:C. To assess relationships between the different analytical techniques for stability, the results were plotted against each other in correlation diagrams and presented in Figure 3-5 with accompanying correlation coefficient R values. As stable-C is calculated on a dry ash free basis the results for fixed C, volatile matter and elemental ratios were also converted to a dry ash free basis to minimise variability of ash content between feedstock types. Heating rate was found to have no statistical effect ($P > 0.5$) on fixed C, volatile matter, stable-C and O:C ratio; however a significant effect was observed for feedstock on H:C ratio ($P = 0.007$).

The results from direct oxidation were correlated with H:C and O:C for each individual feedstock as well as a total correlation of all the data. In most cases the correlations were considered to be very strong for all feedstock at both heating rates. Strong correlation between stability indicators for samples produced for the same feedstock does not confirm compatibility between methods for more diverse samples from multiple types of biomass. The differing gradient of correlation coefficients between the feedstock and therefore overall scatter of data points should also be considered when reviewing the compatibility between analytical methods for determining stability.

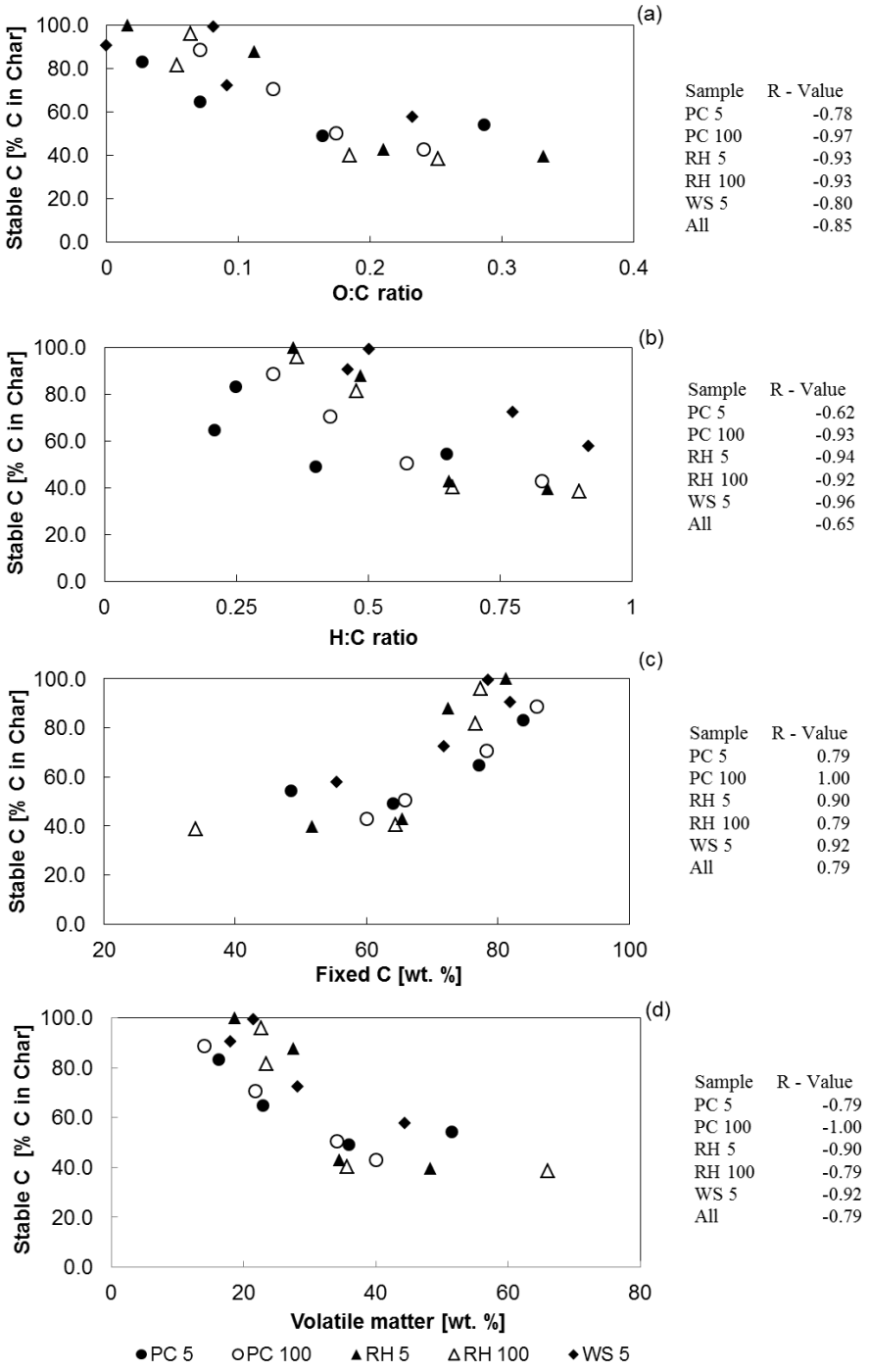

Figure 3-5: Comparison of results between the stable-C tool and alternative methods for biochar stability: proximate and ultimate analysis, (a) stable-C % vs O:C ratio (b) stable-C % vs H:C ratio (c) stable-C % vs fixed C % (d) stable-C % vs volatile matter %.

When comparing the correlation of stable-C vs O:C/H:C for all samples (Figure 3-5), increased scatter of the H:C values resulted in lower correlation coefficients ($R = -0.645$, $P = 0.002$) compared to that for O:C ($R = -0.847$, $P < 0.0001$). This large scatter could be due to the trend previously mentioned (Figure A1-2), where at any of the selected production conditions the H:C ratio follows a decreasing trend of WS > RH > PC. This observed trend indicates that the variation in H:C ratio could be influenced to a greater extent by feedstock properties compared to that of O:C, confirmed by the higher statistical dependency of H:C ($P < 0.0001$) than O:C ($P = 0.064$). The strong influence of feedstock on H:C ratio is derived from the enhanced impact of feedstock on H concentration ($P < 0.0001$, daf) whereas O content is not influenced by feedstock ($P = 0.075$). As seen in Table 3-2 biochar samples produced from PC and RH under the same production conditions contain similar concentrations of C which also applies to WS biochar produced at higher temperatures ($\geq 550^{o}C$). The decreasing trend (WS > RH > PC) of H content present in the biochar samples therefore resulted in higher H:C ratios. The absent effect of feedstock on O content could stem from its determination based on subtraction rather than analytical measurement of the O concentration. This approach can lead to inaccuracy in the quantification of O due to assumptions made over the composition of biochar. Therefore O derived data can influence the correlation with other measures of stability while failing to demonstrate the significance of external factors such as feedstock.

Strong correlation was observed when comparing direct oxidation with fixed C or volatile matter for each feedstock and heating rates ($R = 0.793$, $P < 0.0001$) (Figure 3-5). Identical R values were observed for both graphs demonstrating the relationship between decreasing volatile matter and the resulting increase in fixed C concentration. The overall spread of data within both graphs is potentially due to the influence of the varying ash concentration of high (RH), medium (WS) and low (PC) present in the char samples as well as any impact of heterogeneous feedstock samples. The correlation between the varying methods could also be influenced by the volatilisation of ash components during proximate analysis.

Correlations between the more established analytical methods for stability of fixed C vs O:C, fixed C vs H:C, volatile matter vs O:C and volatile matter vs H:C were carried out and shown in Appendix 1 (Figure A1-3). Strong correlations were again demonstrated for each feedstock at both heating rates as well as the total correlation of the whole data set ($R \geq 0.93$). Overall correlation values were representative of weaker correlation when comparing proximate data against H:C ($R = -0.806$, $P < 0.0001$) rather than against O:C ($R = -0.888$, $P < 0.0001$) however both correlations were determined to be strong. Increased scatter can be seen in graphs comparing fixed C/volatile matter with H:C ratio, similar to that shown in Figure 3-5, although not to as great an extent, demonstrating the larger spread in H:C for all biochar samples and reiterating the impact of feedstock on H:C determination. Samples for which divergence is observed between methods, or where the scatter in the relationship is enhanced, can provide clues for revealing the strength, mode and susceptibilities of each method to external influences and therefore evaluate the comparison with soil conditions when biochar will ultimately degrade.

3.4 Conclusion

A new method of direct chemical oxidation of biochar, alongside three candidate methods for determination of relative biochar stability, i.e. fixed carbon content, O:C and H:C ratios, was applied to a systematic set of biochar samples to indicate their relative stability. The results showed that HTT had the strongest effect on biochar stability, with stability increasing as HTT was elevated. However HTT was shown to have less effect on the yield of stable-C for biochar prepared from low ash feedstock (PC and WS) while the stable-C yield of biochar produced from RH (high ash biomass) was seen to substantially increase above 450^{o}C creating two levels for stable-C yield between 350^{o}C – 450^{o}C and 550^{o}C – 650^{o}C. Therefore increasing the pyrolysis HTT could be utilised to provide additional benefits such as structural, chemical and energy generation without sacrificing the C sequestration potential of biochar.

Comparison of results from direct oxidation of biochar with stability indicators derived from proximate and ultimate analysis showed a strong correlation between the approaches across feedstock and production conditions (pyrolysis temperature and heating rate). However, despite the strong correlations, there was a sufficient degree of scatter, as well as indication of different sensitivities to feedstock properties, that would reduce the usability of these correlations for predictive purposes. The results of this paper aim to highlight the sensitivity of the current methods for stability assessment, while proving valuable in defining protocols for defining stability or developing new improved methods.

The analysis of a systematic set of biochar samples generated using a small-scale batch pyrolysis unit capable of accurately replicating production conditions allowed for the detailed investigation of how biochar properties, in particular stable-C yield, change with process conditions. Through comparing different techniques for assessing the stability of biochar, a better understanding of the assessment potential of the stable-C tool could be achieved, while also gaining important information about which process conditions play a dominant role when determining the C

sequestration potential of biochar (Objective 1). However the reproducibility of these results and therefore correlation between techniques could quite possibly vary greatly depending on the pyrolysis unit as well as scale of production. Therefore the collection and analysis of samples from various pyrolysis units on differing scales using a variety of production conditions would utilise a wider range of variables which could then be statistically analysed for significance to biochar properties, and used as calibration to improve the prediction of biochar stability in soil. Such a study, where the direct oxidation method was applied to a larger sample set consisting of biochar produced from various types of biomass and pyrolysis units, is presented in Appendix 3.

Chapter 4. **Biochar – synergies and trade-offs between soil enhancing properties and C sequestration potential**

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The candidate, as lead author, was solely responsible for all experimentation, laboratory analysis (unless stated otherwise), data analysis and writing of the paper. Co-authors provided guidance and support on the scope and design of the project, the analyses performed and contributed to the editing of the manuscript. Clare Peters and Andrew Cross also provided assistance during stages of the laboratory analysis.

Abstract

The characterisation of biochar has been predominantly focused around determining physicochemical properties including chemical composition, porosity, and volatile content. To date, little systematic research has been done into assessing the properties of biochar that directly relate to its function in soil and how production conditions could impact these. The aim of this study was to evaluate how pyrolysis conditions can influence biochar's potential for soil enhancing benefits by addressing key soil constraints, and identify potential synergies and restrictions. To do this, biochar produced from pine wood chips (PC), wheat straw (WS) and wheat straw pellets (WSP) at four HTTs (350^{o}C, 450^{o}C, 550^{o}C and 650^{o}C) and two heating rates (5^{o}C min^{-1} and 100^{o}C min^{-1}) were analysed for pH, extractable nutrients, CEC, stable-C content and labile-C content. HTT and feedstock selection played an important role in the development of biochar functional properties while overall heating rate (in the range investigated) was found to have no significant effect on pH, stable-C or labile-C concentrations. Increasing the HTT reduced biochar yield and labile-C content while increasing the yield of stable-C present within biochar. Biochar produced at higher HTT also demonstrated a higher degree of alkalinity improving biochar's ability to increase soil pH. The concentration of extractable nutrients was mainly affected by feedstock selection while the biochar CEC was influenced by HTT, generally reaching its highest values between 450^{o}C – 550^{o}C. Biochar produced at $\geq$ 550^{o}C showed high combined values for C stability, pH and CEC while lower HTTs favoured nutrient availability. Therefore attempts to maximise biochar's C sequestration potential could reduce the availability of biochar nutrients. Developing our understanding of how feedstock selection and processing conditions influence key biochar properties can be used to refine the pyrolysis process and design of "bespoke biochar" engineered to deliver specific environmental functions.

4.1 Introduction

Applying biochar to soil has been proposed to improve soil fertility (Chan & Xu, 2009; Atkinson *et al.*, 2010) while sequestering carbon (Lehmann, 2007; Sohi *et al.*, 2010; Ippolito *et al.*, 2012; Manyà, 2012) and reducing or supressing the release of GHG such as CO_2, N_2O and CH_4 (Spokas & Reicosky, 2009; Zhang *et al.*, 2010; Bruun *et al.*, 2011). Due to the large variety of biomass potentially available for conversion to biochar, as well as different pyrolysis technologies (thermal, microwave etc.) and possible processing conditions (temperature, heating rate, vapour residence time etc.), an infinite range of biochar types could be created. These will differ in their physicochemical properties and functional performance (Verheijen *et al.*, 2009; Enders *et al.*, 2012; Ronsse *et al.*, 2013). While the influence of production conditions on the physiochemical properties of biochar has been widely covered (Williams & Besler, 1996; Antal & Grønli, 2003; Demirbas, 2006a; Shackley & Sohi, 2010; Enders *et al.*, 2012; Angin, 2013) little has been reported on the corresponding effects on biochar functional properties (Atkinson *et al.*, 2010; Rajkovich *et al.*, 2011; Crombie *et al.*, 2013; Mašek *et al.*, 2013a). Functional properties are those which could contribute to soil water holding capacity, crop nutrient availability, carbon storage, CEC, pH, etc.

Biochar has been consistently shown to be recalcitrant (Spokas, 2010; Enders *et al.*, 2012; Crombie *et al.*, 2013) when applied to soil which is its most important property in terms of C sequestration potential. Although having high levels of resistance, biochar is still gradually mineralized to CO_2; otherwise, SOM would be dominated by biochar accumulated over long time scales (Masiello, 2004; Cheng *et al.*, 2006; Lehmann *et al.*, 2008). Therefore the absolute longevity of biochar in soil cannot be quantified by one number as biochar is not one consistent homogeneous state (Hedges *et al.*, 2000). Different fractions and pools of biochar will decompose at different rates under different conditions determined by method of production and starting material, as well as climate and soil properties. This makes the quantification of stability and degradation rates extremely important to the environmental and economic feasibility of biochar production. Direct measurements of stability on the

timescale of decades or even a century is not possible, leading to the development of laboratory based assessment tools for the rapid screening of fresh biochar (Hammes *et al.*, 2007; Cross & Sohi, 2011, 2013; Harvey *et al.*, 2012; Crombie *et al.*, 2013).

After low temperature pyrolysis, biochar may contain an unconverted or partially converted biomass fraction, known as labile-C, which is rapidly mineralized on addition to soil. The mineralization of labile-C results in a small short term CO_2 flux (Zimmerman, 2010; Bruun *et al.*, 2011; Calvelo Pereira *et al.*, 2011; Cross & Sohi, 2011; Jones *et al.*, 2011) and could be responsible for mineralization of other soil C, i.e. priming (Hamer *et al.*, 2004; Cross & Sohi, 2011; Jones *et al.*, 2011; Lehmann *et al.*, 2011; Zimmerman *et al.*, 2011). However, labile-C can also provide a readily available food source for soil microorganisms (Smith *et al.*, 2010). However this stimulated microbial activity occurs over a short time period (Cheng *et al.*, 2006) with long incubation tests actually showing decreased or no mineralization of other soil C following biochar application (Kuzyakov *et al.*, 2009; Spokas & Reicosky, 2009; Zimmerman, 2010; Cross & Sohi, 2011; Zimmerman *et al.*, 2011). In many cases the observed release of CO_2 from biochar takes place over a relatively short period of weeks or months before dissipating (Smith *et al.*, 2010; Jones *et al.*, 2011). However the inconsistency in CO_2 evolution following the addition of biochar to soil could be a result of large variability in the nature of applied biochar (feedstock, temperature, heating rate, pre/post treatment) as well as the conditions used during incubation studies (temperature, soil type, incubation time, atmosphere, pH) (Jones *et al.*, 2011; Zimmerman *et al.*, 2011), making conclusions on the positive or negative aspects of labile-C difficult.

Many studies have reported the effectiveness of biochar in improving soil quality and crop production (Lehmann *et al.*, 2006; Liang *et al.*, 2006; Laird, 2008; Atkinson *et al.*, 2010; Van Zwieten *et al.*, 2010; Rajkovich *et al.*, 2011; Ippolito *et al.*, 2012; Spokas *et al.*, 2012; Liu *et al.*, 2013). The positive impact of biochar could be due to a range of potential reactions that remove soil-related constraints otherwise limiting plant growth: soil nutrient status and soil pH, toxins, improved soil physical properties and improved N-fertilizer use efficiency (Chan & Xu, 2009; Van Zwieten

et al., 2010). As biochar is produced by thermal carbonisation of biomass (virgin and non-virgin), it often contains a high concentration of C, as well as varying amounts of plant macro nutrients (phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca) etc.) and micro nutrients (iron (Fe), copper (Cu), sodium (Na), zinc (Zn), chlorine (Cl) etc.) (Chan & Xu, 2009; Lehmann *et al.*, 2011). However the total concentration of nutrients within biochar is not necessarily an appropriate indicator of the content of bioavailable nutrients, as many can be bound in stable forms not readily available to plants (Chan & Xu, 2009; Spokas *et al.*, 2012). CEC is the capacity of biochar to retain cations in a plant-available and exchangeable form (e.g. nitrogen in the form of ammonium, NH_4^+). The CEC is relatively low at low (acidic) pH but increases at higher pH as well as generally being very low at low HTT with substantial improvement as temperature is increased (Lehmann, 2007). While freshly produced biochar demonstrates minimal CEC compared to SOM, biochar has shown the ability to increase its CEC upon addition to soil through abiotic and biotic oxidation and the adsorption of SOM onto its surface (Cheng *et al.*, 2006; Liang *et al.*, 2006; Lehmann, 2007).

Increasing the CEC of biochar can result in reducing the leaching of nutrients (e.g. P, ammonium, nitrate, Mg and Ca) from soil, manure, slurry etc. thus increasing the potential availability of nutrients in the root zone for plant uptake and improved soil fertility (Glaser *et al.*, 2001; Chan & Xu, 2009; Major *et al.*, 2009; Clough & Condron, 2010; Angst *et al.*, 2013). Furthermore, by improving the sorption ability of biochar, the efficiency of fertilizer can be increased by absorbing it to the biochar thus improving its retention in the root zone for uptake by plants (Chan & Xu, 2009; Xu *et al.*, 2013). Increasing the N-fertilizer use efficiency can then lead to a reduction in fertilizer application rates, thus decreasing GHG emissions associated with fertilizer production, transport etc. (Major *et al.*, 2009) as well as the direct release of GHG (Zhang *et al.*, 2010). However, adding biochar to soil does not necessarily guarantee a related increase in the CEC of the soil. While some studies have shown a positive increase in soil pH and CEC following the incorporation of biochar into soil other studies have shown the opposite effect (Van Zwieten *et al.*,

2010). There are relatively few studies on the nutrient composition of biochar and its importance to soil amendment (Atkinson *et al.*, 2010; Rajkovich *et al.*, 2011; Angst & Sohi, 2013; Xu *et al.*, 2013; Zheng *et al.*, 2013) and less concerning how production conditions can influence the nutrient content of biochar and their availability (Zheng *et al.*, 2013).

Therefore, this work builds on Chapter 3 by continuing to investigate the relationship between production conditions and the C mitigation potential of biochar as well as additional functional properties related to the soil enhancing benefits of biochar such as labile-C concentration, pH, CEC and biochar nutrient availability. Through this the chapter aims to improve the understanding of how selected production conditions impact the effectiveness of biochar for soil amendment (Objective 1) while also identifying possible or impossible combinations of functional properties (Objective 3). By investigating both the soil amendment and C sequestration potential of biochar a better understanding of the trade-off between these two benefits (Objective 3) can refine the process conditions to maximise the environmental potential of biochar (Objective 5).

4.2 Materials and methods

4.2.1 Feedstock

Biochar samples were produced using three types of biomass: mixed pine wood chips (PC), raw wheat straw (WS) and wheat straw pellets (WSP). The full details of feedstock particle size, moisture content and supplier can be found in Table 2-1 in section 2.3.1. Results from ultimate and proximate analysis of the selected materials are also located in section 2.3.1 in Table 2-2. The natural heterogeneity of the feedstock was minimized as far as possible by thoroughly mixing a volume sufficient for all experiments.

4.2.2 Pyrolysis equipment

The experimental set up of the pyrolysis equipment was described in section 2.3.1and shown in Figure 2-1.

4.2.3 Pyrolysis conditions

For each pyrolysis experiment a standard volume of feedstock (approximately 200 mm bed depth) was used, resulting in a different mass of starting material used for each biomass type: 40 g for PC, 15 g for WS and 120 g for WSP. Each type of feedstock was exposed to HTTs of 350^{o}C, 450^{o}C, 550^{o}C and 650^{o}C and two heating rates of 5^{o}C min^{-1} and 100^{o}C min^{-1}. All runs were performed using one standard carrier gas flow rate (0.33 $\pm$ 0.02 L min^{-1}) of nitrogen (N_2) and holding time at HTT (20min). For experiments carried out using the higher heating rate (100^{o}C min^{-1}) the mass of WSP material was reduced to 60 g so that rapid gas release did not exceed the handling capacity of the condensation system. No pyrolysis run could be performed for WSP biomass at 350^{o}C and 100^{o}C min^{-1}, due to aborted pyrolysis runs which resulted in an insufficient amount of remaining homogenous WSP material.

4.2.4 Product analysis

Detailed descriptions of the analytical procedures carried out during this work can be found in section 2.4. In brief, char samples were analysed using proximate analysis (section 2.4.1.1), ultimate analysis (section 2.4.1.2), biochar pH (section 2.4.2.2),

CEC (section 2.4.2.3), extractable nutrients (section 2.4.2.3) as well as the Edinburgh tool kit for stable-C (section 2.4.2.1.1) and labile-C (section 2.4.2.1.2) concentrations.

4.3 Results and discussion

The focus of this work was the assessment of biochar functional properties. Results for pyrolysis product distribution as well as biochar physiochemical properties are therefore reported in Appendix 1 (Table A1-1).

4.3.1 Biochar functional properties

The progress of large scale biochar application to soil has been limited by uncertainties over the response of crops to biochar in the soil. Carbon sequestration, CEC, nutrient content and availability and pH were identified as important properties to investigate and relate to production parameters.

4.3.1.1 Long term biochar stability

The most accurate method of assessing the C sequestration potential of biochar could possibly be through long-term field experiments monitoring stability and degradation over time; however this is not feasible over a period of 100 years or more. In this work we used an oxidation approach (section 2.4.2.1.1) to determine stable-C content (biochar C basis) and yield of stable-C (feedstock C basis). The results plotted in Figure 4-1 show that HTT was the main factor ($P < 0.0001$) determining the concentration and yield of stable-C together with feedstock ($P < 0.026$). On the other hand, no effect was observed for heating rate ($P > 0.05$), in the range investigated. Increasing the pyrolysis HTT generally resulted in an increase in stable-C present within biochar. At HTT < 450^{o}C the slower heating rate produced higher stable-C concentrations compared to 100^{o}C min^{-1} however at higher HTT this trend disappeared as temperature played the dominant role, agreeing with similar trends seen in Chapter 3, Chapter 5 and Antal & Grønli (2003) work.

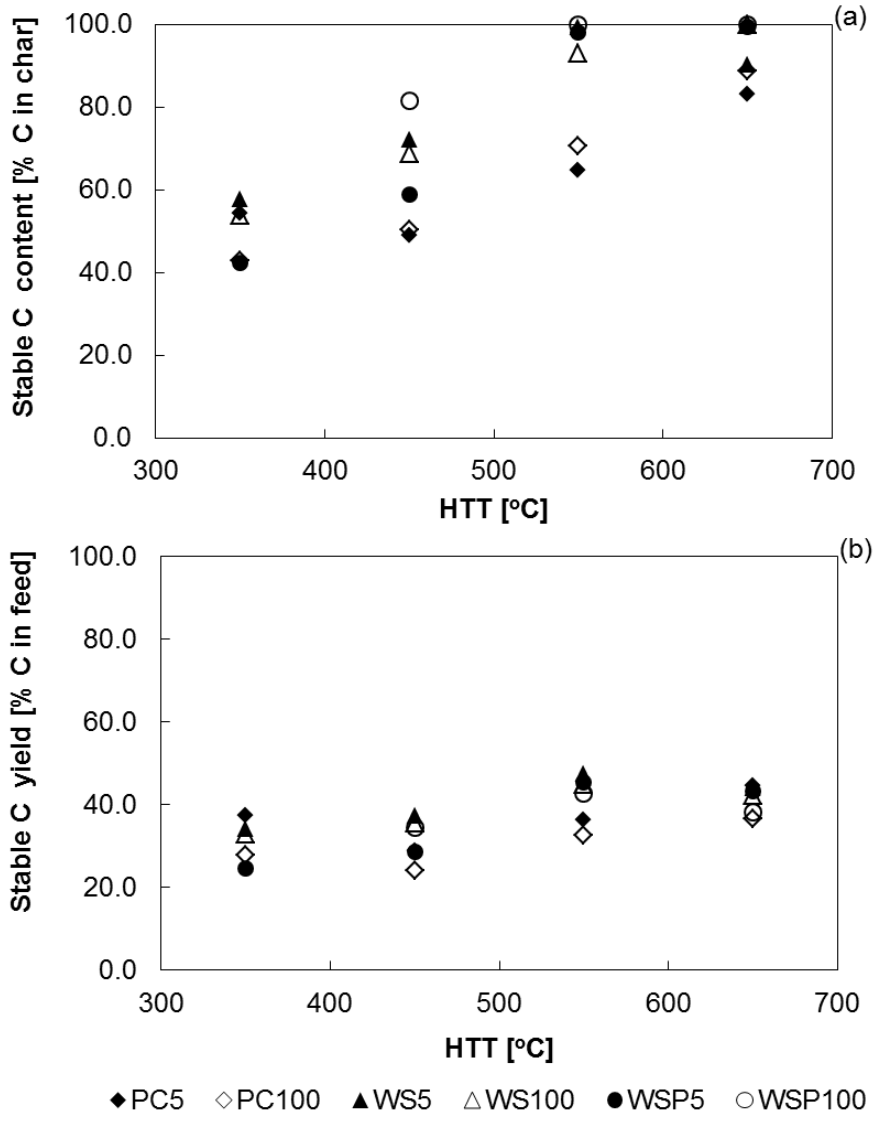

Figure 4-1: Environmental stability of PC, WS and WSP char expressed on (a) char carbon basis (b) feedstock carbon basis. Error bars were added to the graph to show standard error of stable-C %, but are not visible due to the scale of the data (*n* = 3).

The results further showed that the efficiency of conversion of feedstock C into stable C (stable-C yield) increased with HTT, therefore indicating that high HTT improved the C storing potential of biochar, again reaffirming the same trends seen in Chapter 3 and 5 for additional feedstock. The variation in stable-C yield from 350^{o}C – 650^{o}C was considerably lower than that experienced for stable-C concentration with the average difference being 10.7 $\pm$ 4.57 % compared to 42.1 $\pm$

11.4 % for stable-C content. Lower variation in the yield of stable-C as HTT is increased can have a large impact on the economic and environmental case for biochar production, especially when pyrolysis at higher temperatures could provide additional energy and C sequestration benefits (investigated further in Chapter 5). Although there is a significant effect of HTT and feedstock on the stable-C content and stable-C yield, the extent of this influence varies at different heating rates. Both parameters are largely significant when using heating rate of $100^{o}C\ min^{-1}$ ($P < 0.019$), but only HTT shows a statistically significant effect ($P < 0.037$) when applying the lower heating rate ($5^{o}C\ min^{-1}$) ($P < 0.037$), while feedstock type is not significant ($P > 0.147$). The lower heating rate would increase the duration of chemical reactions occurring during pyrolysis and could result in more time for the dominating effect of HTT to influence the biochar stability, causing similar stable-C yields to be obtained for PC, WS and WSP biochar produced at $650^{o}C$.

4.3.1.2 **Biochar labile-C content**

Biochar labile-C content is mainly affected by the HTT ($P < 0.0001$) and feedstock ($P < 0.028$) selection, as shown in Figure 4-2, while heating rate had no statistically significant effect. As the pyrolysis HTT was increased from $350^{o}C$ to $650^{o}C$ the labile-C content in biochar dropped dramatically for WS and WSP feedstock, while PC labile-C content also dropped between $450^{o}C$ and $650^{o}C$. The trend for PC biochar labile-C content was difficult to determine as HTT was increased from $350^{o}C$ to $450^{o}C$ due to a large standard deviation for that biochar sample. All biochar samples produced at $650^{o}C$, with the exception of WS, showed a labile-C content of < 0.11 %. WS biochar produced at $650^{o}C$ contained a labile-C concentration of 0.31 % which was unexpectedly high but not statistically different to the labile-C content (0.18 %) of WS biochar produced at $550^{o}C$.

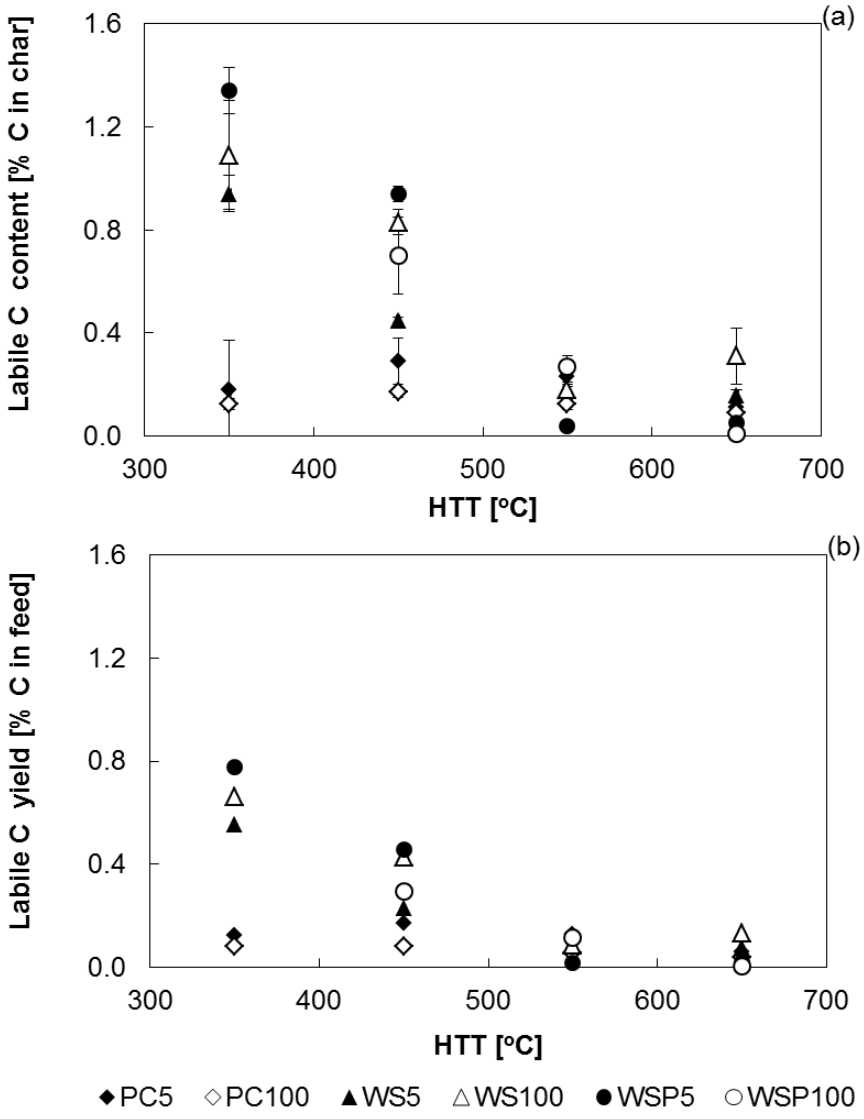

Figure 4-2: Labile C content of PC, WS and WSP biochar expressed on (a) char carbon basis (b) feedstock carbon basis. Error bars were added to the graph to show standard error of labile-C % (*n* = 4).

The initial release of CO_2 when biochar is added to soil could be due to microbial decomposition of an easily degradable C fraction remaining in higher concentrations within low HTT biochar due to incomplete conversion (Cheng *et al.*, 2006; Zimmerman, 2010; Bruun *et al.*, 2011; Calvelo Pereira *et al.*, 2011). However it has also been suggested that CO_2 release could be due to large concentrations of carbonates present in high-ash feedstocks (Enders *et al.*, 2012) as well as the release of sorbed CO_2 on the surface of biochar (Bruun *et al.*, 2014), and therefore can lead

to an over-estimation of biochar C mineralization. These carbonates can be present in the original feedstock or formed during pyrolysis (Smith *et al.*, 2010; Jones *et al.*, 2011; Lehmann *et al.*, 2011; Bruun *et al.*, 2014). There was a clear difference in the concentration of labile-C present within biochar produced from the different feedstock at 350^{o}C with the largest being WSP (1.34 %) followed by WS (0.94 %) and lastly PC (0.18 %). Biochar made from grasses has generally been found to degrade faster than wood biochar and has a higher initial CO_2 flux (Zimmerman *et al.*, 2011).

Similar to labile-C concentration, the labile-C yield (feedstock C basis) of biochar decreased with increasing HTT (Figure 4-2). Biochar produced at $\geq$ 550^{o}C contained a labile-C yield of < 0.14 %, and all biochar samples produced from PC, WS and WSP showed a labile-C yield of $\leq$ 0.17 %, $\leq$ 0.66 %, $\leq$ 0.77 % respectively. Overall this pathway for the release of CO_2 represents only a small fraction of biochar C and therefore does not compromise the C sequestration potential. The observed increase in stable-C yield and decrease in labile-C yield with increasing HTT emphasises that pyrolysis at higher temperatures can sequester more C by increasing the C fraction stable over long periods of time while at the same time reducing the C fraction susceptible to rapid decay. However, further studies into the positive impacts of labile-C (e.g. food source for microorganisms) on soil processes is needed to gain a better understanding of the desired threshold for biochar labile-C content.

4.3.1.3 **Biochar nutrient concentration**

The concentrations of feedstock and biochar extractable nutrients (also referred to as available nutrients) were determined through ammonium acetate extraction (section 2.4.2.3) and shown in Table 4-1 and Table 4-2 respectively. The extraction procedure was originally designed for analyzing soil samples, and so analyzing biochar has demonstrated some limitations of the technique, such as a higher concentration of nutrients being extracted from biochar compared to feedstock. This effect can also be due a dramatic change in physical (surface area, pore volume etc.) and chemical (surface charge, nutrient form etc.) properties following the pyrolysis process.

Table 4-1: Concentration of nutrients extracted from the PC and WSP feedstock via ammonium acetate.

Sample	Extractable Nutrients [mg/kg]						
	Ca	K	Mg	Na	Total P	Exctracted P	CEC [$cmol_c$/kg]
Pine	648.0	787.0	162.7	422.5	146.0	174.0	51.0
Wheat Pellets	1873.0	1969.0	213.7	401.1	335.0	206.0	117.0

Table 4-2: The ash content (db), CEC and extractable nutrient concentrations of biochar produced from PC, WS and WSP feedstock.

Sample	Extractable Nutrients							
	Ash [wt.%, db]	Extracted biochar Nutrient / Extracted Feed Nutrient [%]					Extracted Biochar P / Total Biochar P [%]	CEC [$cmol_c$/kg]
		Ca	K	Mg	Na	P		
PC350/5	1.4	5.3	4.3	7.7	34.1	12.8	21.5	35.7
PC450/5	2.9	10.3	13.8	9.5	34.5	9.8	17.4	60.6
PC550/5	4.2	4.5	4.1	4.9	22.0	9.2	14.0	65.9
PC650/5	5.9	6.6	13.6	5.5	21.5	7.2	9.0	41.4
PC350/100	3.4	5.6	8.8	6.7	28.7	17.0	15.3	38.4
PC450/100	3.4	10.1	12.6	5.3	19.1	8.0	13.9	48.0
PC550/100	0.7	11.2	18.9	5.5	18.9	4.5	5.1	32.9
PC650/100	5.0	13.8	36.8	5.9	20.1	9.4	12.8	27.5
WSP350/5	14.4	22.8	17.2	16.5	40.7	87.0	82.1	30.7
WSP450/5	17.6	100.0	100.0	69.9	80.2	100.0	100.0	72.5
WSP550/5	20.1	24.1	84.3	12.8	53.3	89.5	85.8	27.4
WSP650/5	21.9	51.7	100.0	21.1	68.4	44.5	44.5	79.6
WSP350/100	-	-	-	-	-	-	-	-
WSP450/100	20.9	12.7	24.1	9.0	26.1	82.2	78.2	36.8
WSP550/100	21.9	8.2	22.1	5.6	24.7	65.0	61.2	60.6
WSP650/100	23.7	4.7	15.7	4.4	25.3	24.5	22.0	46.7

4.3.1.3.1 **Extractable nutrients**

The mineral content of biochar consists largely of nutrients such as P, K, Ca, Mg, Cl, Na etc. which can cause a catalytic effect during pyrolysis affecting the yields, composition and properties of char, condensable liquids and gas co-products including the reactivity and ignition properties of chars (Antal & Grønli, 2003; Sonoyama *et al.*, 2006; Mašek *et al.*, 2007; Brown, 2009; Enders & Lehmann, 2012). As the majority of feedstock nutrients are retained in the ash fraction of biochar, and the ash concentration of biochar increases with rising HTT, a strong positive correlation can be seen between ash content and the amount of extractable K (R^2 = 0.713, P = 0.003) while moderate correlations are also evident for Ca (R^2 = 0.632, P = 0.011), Na (R^2 = 0.601, P = 0.018) and Mg (R^2 = 0.541, P = 0.037). The amount of extractable nutrients was also considerably higher for the high ash WSP biochar compared to the relatively low ash PC biochar (Table 4-2). Due to this clear correlation of ash content with nutrient composition, the selection of feedstock was deemed to be the determining factor in the final biochar concentration of K (P = 0.005) and Na (P = 0.014); however Ca (P = 0.070) and Mg (P = 0.139) overall were not influenced by feedstock selection (for the types investigated). Although the influence of feedstock is clear, it is not surprising as only two types of feedstock, which differ greatly in origin and composition, were used for the comparison.

The concentrations of Ca, K, Mg and Na extracted from WSP biochar generally peak at 450^{o}C for both heating rates with increased HTT, resulting in equal or lower concentrations of nutrients. The concentration of extractable nutrients from WSP biochar was substantially smaller when the higher heating rate was applied. This could be due to a loss of biochar structure and decrease in pore volume caused by a combination of a high heating rate and ash content (Downie *et al.*, 2009). A lack of structure in biochar produced using higher heating rates has been attributed to the melting of the cell structure and the blocking of pores (Downie *et al.*, 2009). Increasing the heating rate of pyrolysis reduces the time available for volatiles to be discharged during pyrolysis, leading to a shorter time for pore development, as well as increasing the accumulation of volatiles between and within particles (Luo *et al.*, 2010; Angin, 2013). For PC biochar, the highest amount for nutrient extraction

occurred at 450^{o}C when using the low heating rate; however pyrolysis of PC at a higher heating rate resulted in increasing nutrient extraction with increasing HTT. This led to the peak nutrient extraction for Ca, K and Na all occurring at 650^{o}C. The ash content of PC biochar is considerably lower than WSP biochar, therefore the expected loss of structure due to the presence of ash would be minimal.

4.3.1.3.2 **Phosphorus**

Total biochar P and extractable P concentrations are also shown in Table 4-2. Firstly to assess the yield of P extracted from the initial feedstock sample, the amount of extractable P (biochar weight basis) from biochar was expressed as a percentage of the extracted feedstock P. Secondly the amount of extractable biochar P was further expressed as a percentage of the total biochar P (biochar weight basis) to determine the proportion of P remaining within the biochar sample. For the range of process conditions investigated, the yield of extractable P as a function of extracted feedstock P peaked at 350^{o}C for PC biochar and 450^{o}C for WSP for both heating rates while the yield of extractable P as a function of total biochar P also peaked under the same conditions. The extractable P concentration for WSP biochar at 450^{o}C actually exceeded the total P measurement for that biochar sample. This can be caused by a lack of repeated analysis or limitations of the total P extraction method. WSP was previously seen to contain a higher amount of extractable Ca, K, Mg and Na compared to PC biochar; this trend applied also to P. It is desirable to retain as many nutrient elements in biochar as possible. For some elements a proportion are lost by vaporisation during pyrolysis (K, Na, S, N etc.) with over half of their content being released at temperatures below 500^{o}C (Mašek *et al.*, 2007; Chan & Xu, 2009; Enders *et al.*, 2012). A lack of P volatilization compared to other nutrients as HTT is increased could be the reason for a rise in total P as pyrolysis HTT is increased. Although total biochar P concentration increases with HTT, P availability can decrease due to P being trapped in less available forms at higher temperatures (Chan & Xu, 2009). To maintain content and availability of crop nutrient elements the preferred temperature of pyrolysis, based on the results of this work, would be between 450^{o}C – 550^{o}C which falls within the range put forward by Chan & Xu

(2009) (400^{o}C – 500^{o}C). The exact conditions for improved nutrient properties may well differ between feedstock.

4.3.1.3.3 Cation exchange capacity

In addition to the extracted nutrient concentrations, the CEC of biochar samples were also determined and shown in Table 4-2. In the HTT range 350^{o}C to 650^{o}C, biochar CEC increased between 450^{o} – 550^{o}C for both feedstocks at both heating rates. This was consistent with trends reported previously (Lehmann, 2007). However, as HTT was increased to 650^{o}C, CEC decreased for all samples (except WSP biochar produced using 5^{o}C min^{-1}) potentially due to a reduction in surface area attributed to the higher pyrolysis HTT. Since the biochar structure becomes more aromatic at higher pyrolysis temperatures, large amounts of acid-base surface functional groups (Chan & Xu, 2009; Lehmann *et al.*, 2011) are lost, altering the charge of biochar (Novak *et al.*, 2009; Lehmann *et al.*, 2011) and thereby influencing the nutrient retention ability of cations and anions determined by CEC and AEC (Chan & Xu, 2009).

4.3.1.4 Biochar pH in solution

Some studies have indicated that ash content of feedstock in conjunction with pyrolysis severity could influence the final pH of biochar samples (Glaser *et al.*, 2002; Lehmann *et al.*, 2011; Enders *et al.*, 2012; Ronsse *et al.*, 2013; Novak *et al.*, 2014). Enders *et al.* (2012) suggested that a large proportion of the ash in high-ash feedstock contains carbonates which could cause a liming effect. While the production conditions of feedstock and HTT are well covered throughout these studies, the impact of heating rate has not been covered. HTT ($P < 0.0001$) and feedstock selection ($P < 0.0001$) were both seen to influence the final pH value of biochar, while heating rate only influenced the pH value of PC biochar. As the HTT of pyrolysis increased so too did the biochar pH, as seen in Figure 4-3, indicating that higher HTT results in biochar with increased alkalinity. Studies have shown that, under less severe pyrolysis conditions (reduced HTT and heating rate), more labile and oxygenated carbon with high acid-base surface functional groups are retained in

the char; however as the severity of pyrolysis increased, more acidic groups (e.g. carboxyl) became deprotonated to the conjugate base, consequentially causing a rise in the pH of biochar in solution (Chan & Xu, 2009; Ronsse *et al.*, 2013; Zheng *et al.*, 2013). The pH of biochar has been associated with having a liming effect on soil acidity, thus increasing the soil pH following the addition of biochar (Van Zwieten *et al.*, 2010; Biederman & Harpole, 2013; Liu *et al.*, 2013; Novak *et al.*, 2014). When heating rate of $100^{o}C\ min^{-1}$ was used the pH of PC biochar increased with HTT while the pH values of WS and WSP were not affected ($P > 0.05$) by HTT. Applying the higher heating rate of $100^{o}C\ min^{-1}$ can increase the rate at which volatiles are released from biochar, thus affecting the rate that the deprotonation of the acidic groups within biochar occurs, resulting in similar pH values over the temperature range $450^{o}C$ – $650^{o}C$ compared to $5^{o}C\ min^{-1}$.

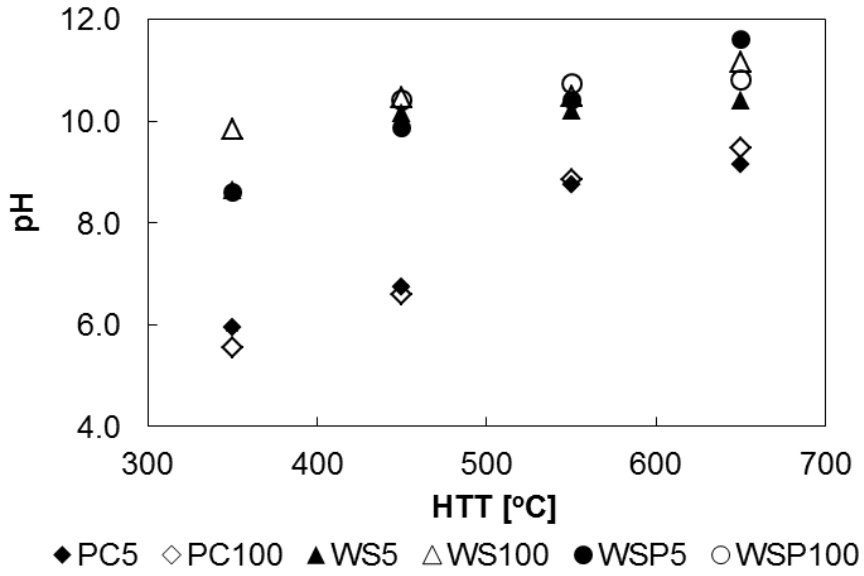

Figure 4-3: Investigating the effect of temperature and heating rate on the pH of biochar. Error bars were added to the graph to show standard error of biochar pH, but are not visible due to the scale of the data (*n* = 3).

Differences in pH can also be observed between the biomass types: pH of biochar derived from woody biomass was consistently lower compared to straw-based biochar. The higher pH values of WS and WSP biochar over PC biochar can be strongly correlated ($R^2 = 0.891$, $P < 0.0001$) with the larger ash concentration of

wheat biochar compared to wood. The influence of ash can be clearly seen when comparing the values for PC biochar (ash = 0.7 – 5.9 %, pH = 5.5 – 9.1) to that of WS (ash = 10.9 – 27.6 %, pH = 8.6 – 11.2) and WSP (ash = 14.4 – 23.7 %, pH = 8.6 – 11.6). Increasing the alkaline nature of biochar can increase the ability of biochar to improve crop productivity, however a number of variables such as soil type and climate also need to be considered (Czimczik & Masiello, 2007), since application of biochar with a very high pH can also have negative effects on soil such as micronutrient deficiencies (Chan & Xu, 2009).

4.3.2 Assessing the synergies and trade-offs of biochar production

Identifying a combination of production conditions which could maximise the soil enhancing and C sequestering properties of biochar would be practically impossible due to the impact that processing conditions can have on several biochar properties simultaneously. For that reason a fine balance needs to be found between the C mitigation potential of biochar and identifying the functions relevant to the soil constraint being addressed i.e. soil pH, nutrient retention, microbial activity etc. To aid in the identification of these relationships Figure 4-4 (a matrix plot diagram) and Figure 4-5 (combination of scatterplot diagrams) were used to show the ranges in which biochar functional properties can be varied by adjusting key production parameters. In the following section each biochar sample is identified by feedstock-HTT-heating rate e.g. PC-650-5 would refer to biochar produced from PC, using the HTT of 650^{o}C and the heating rate of 5^{o}C min^{-1}.

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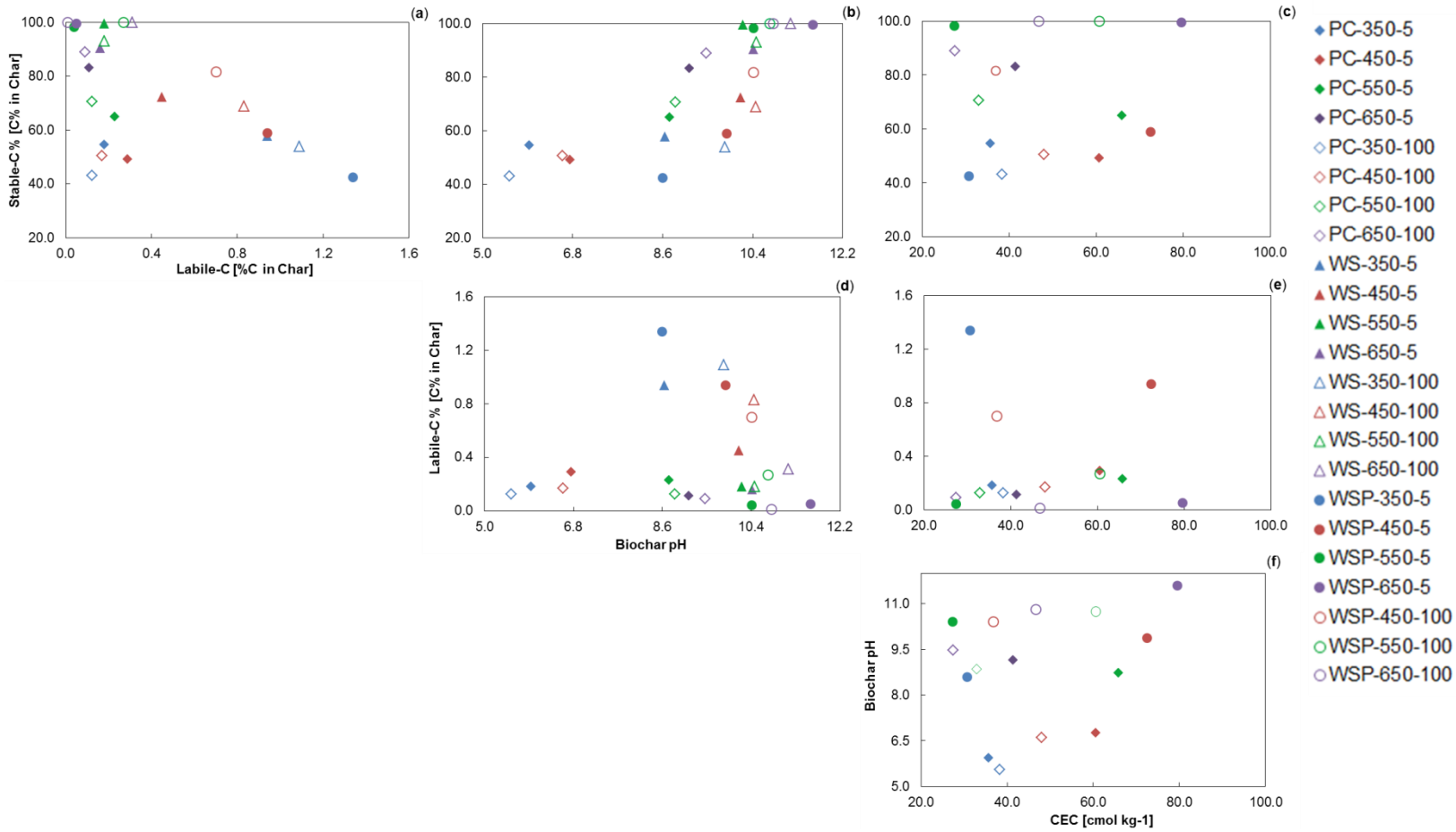

Figure 4-4: Matrix plot comparing biochar functional properties, (a) stable-C vs labile-C (b) stable-C vs pH (c) stable-C vs CEC (d) labile-C vs pH (e) labile-C vs CEC (f) pH vs CEC.

4.3.2.1 Carbon stability versus degradability

If the desired outcome of pyrolysis is to increase the fraction of stored C and minimise the degradable C fraction, then this can be achieved through applying higher pyrolysis temperatures (HTT >550^{o}C), (as seen in Chapter 3 and 5), i.e. WS-550-5, WS-650-5, WS-550-100, WS-650-100, WSP-550-5, WSP-650-5, WSP-550-100, WSP-650-100, PC-650-5 and PC-650-100 (Figure 4-4). Where the concentration of labile-C is an important key soil property a HTT $\leq$ 450^{o}C would result in higher labile-C concentration, however at the expense of long-term C sequestration. Few stable biochar samples contained relatively "high" labile-C content when comparing the entire data set. However WS-450-5 and WSP-450-100 both contained a labile-C content > 0.45 % and stable-C concentrations above 72 %. WSP-450-100 in fact contained a labile-C concentration of 0.70 % and stable-C content of 81.8 %, demonstrating a good combination of relatively high values of both stable-C and labile-C. While labile-C provides an energy source for microbial communities that promote soil aggregation, high-concentrations of labile-C could result in biological immobilisation of soil N which could become problematic if biochar is applied in large quantities. It is important to note that stable-C accounts for the long-term stability of C (> 100 years) while relatively non-stable labile-C demonstrates the short term decomposition of biochar C (two week incubations). Therefore combining stable-C and labile-C does not account for the total C present within biochar, indicating a third fraction of intermediate stability (2 weeks < Int-C < 100 years) (discussed further in Chapter 5). It is important to consider this additional C fraction when assessing the C sequestration potential of biochar since it bridges the gap between the two extremes for biochar C stability, and therefore can influence trade-offs between C mitigation and other important benefits (GHG emissions, soil enhancement etc.).

4.3.2.2 Carbon stability versus liming value

It has been well documented that biochar of high alkalinity has been effective at increasing fertility of acidic soils (Van Zwieten *et al.*, 2010; Biederman & Harpole, 2013; Liu *et al.*, 2013; Novak *et al.*, 2014). The cluster seen in Figure 4-4, representing biochar samples WS-550-5, WS-650-5, WS-550-100, WS-650-100,

WSP-550-5, WSP-650-5, WSP-550-100 and WSP-650-100, have high stable-C content and an alkaline pH. Within this smaller group the difference in stable-C content ranged from 90.5 – 100 % and pH from 10.2 – 11.6. A second group of biochar samples which showed less favourable but still relatively high values of stability (81.7 – 88.9 %) and pH (9.1 – 10.4) consisted of PC-650-5, PC-650-100, WSP-450-100. Although PC-650-100 was identified as having a high stable-C concentration (88.9 %) its pH value of 9.14 was lower than the WS and WSP biochar produced at HTT > 550^{o}C. However a pH of this value could still potentially provide an effective soil response, depending on site specific soil properties. Furthermore, since labile-C decreases linearly with increasing HTT, any attempt to maximise the pH of biochar and stable-C concentration would result in a reduction in the labile-C content e.g. WSP-650-5 biochar produced the highest biochar pH but also contained the second lowest labile-C concentration (Figure 4-4). Any reduction in HTT led to a reduction in pH and an increase in the concentration of labile-C. While it was clearly identified that increasing the severity of pyrolysis resulted in higher pH values and C stability, for soil amendment, biochar with a high pH value may not be preferable. Too high a pH has been shown to cause micronutrient deficiencies (Chan & Xu, 2009). Therefore determining the ideal pH value for biochar will undoubtedly be influenced by the initial pH of the soil and the effect that biochar pH has on the overall agronomic impact of biochar.

4.3.2.2.1 **Carbon stability versus CEC**

Non-linear progression of CEC with HTT made production conditions that maximise both stable-C concentration and CEC difficult to define (Figure 4-4). The surface area and CEC of biochar has typically been shown to decrease when made at HTT > 550^{o}C, and to maximise the CEC value, pyrolysis should be performed at temperatures between 500 – 550^{o}C (Lehmann, 2007). However CEC for PC and WSP biochar reached its highest values between 450^{o}C and 550^{o}C, depending on the applied heating rate. Therefore, this indicates that the preferred pyrolysis temperature could actually fall between 450^{o}C and 550^{o}C. Too high a temperature can cause greater surface area, increased aromatic structure and loss of negative charge, and therefore decrease the CEC (Novak *et al.*, 2009; Lehmann *et al.*, 2011).

When comparing the biochar CEC with stable-C concentration (Figure 4-4) some biochar samples show a high value for CEC but low stable-C content (WSP-450-5) or vice versa (WSP-550-5). Biochar produced from WSP at 650^{o}C using 5^{o}C min^{-1} (WSP-650-5) demonstrated the highest CEC while also containing a high stable-C concentration of 99.5 %. With the exception of WSP-650-5, the CEC of biochar tended to be higher at HTT $\leq$ 550^{o}C. Despite the importance of CEC, due to the fact that in general the initial CEC of fresh biochar is low, the importance of this parameter for optimisation is limited. It is the ability of biochar to acquire high CEC upon addition to soil, as a result of abiotic and biotic oxidation (Cheng *et al.*, 2006; Xu *et al.*, 2013) that is more relevant. Therefore while the initial CEC of biochar may be relatively low compared to SOM, the long term influence of CEC on nutrient retention may be an important functional property to monitor.

4.3.2.2.2 Carbon stability versus extractable crop nutrients

Biochar produced from virgin biomass contains a relatively limited amount of nutrients, and therefore cannot be compared to conventional fertilisers. Nevertheless, the ability of biochar to release nutrients is important. The concentration of available plant nutrients in biochar was determined by ammonium acetate extraction. While the high temperature pyrolysis ($\geq$ 550^{o}C) of PC and WSP biomass has consistently shown a high C storage potential, high alkalinity, low labile-C concentration as well as high values of CEC, the concentration of extractable biochar nutrients was highest at 450^{o}C. As HTT is increased from 200^{o}C to 500^{o}C, the greater production of volatile material can enhance pore (macro-, meso- and micro-) development, leading to increased pore volume and surface area (Downie *et al.*, 2009; Angin, 2013). Above 500^{o}C, structural re-ordering, pore widening, pore blockage and melting or fusing of ash seems to predominate, resulting in decreased pore volume and surface area (Downie *et al.*, 2009; Fu *et al.*, 2011) reducing the extractability of plant nutrients. Therefore any beneficial properties obtained at higher HTT may be at a cost of crop nutrient availability. The stable-C concentration of biochar samples was compared to the concentrations of extracted Ca, Mg, K, Na, P and total P in Figure 4-5 and WSP-450-5 was consistently associated with the highest extractable amounts of Ca (100 %), K (100 %), Mg (69.9 %), Na (80.2 %) and P (100 %) as well as the

second highest CEC (72.5 $cmol_c$ kg^{-1}) of any biochar. While the processing conditions used to produce this biochar did give a high pH (9.9), the stable-C content was relatively low (58.9 %) compared to other biochar samples investigated. This highlights the trade-off between C storage versus enhancing soil quality (Jeffery *et al.*, 2013). While WSP-450-5 was associated with the largest amount of extractable nutrients, it was not the only biochar to show positive results for this functional property. The highest extractable P content was found in WSP-550-5 which also contained a stable-C concentration of 98.2 %. This again demonstrates the increased availability of nutrients from biochar produced at HTT $\geq$ 550^{o}C. Two further biochar samples (WSP-650-5 and WSP-550-100) also showed a potentially positive combination of extractable P (> 44.5 %) and stable-C concentration (> 99.5 %). All other biochar samples either contained too low a concentration of stable-C or extractable P. WSP-650-5 also demonstrated a high stable-C (99.5 %) concentration in conjunction with high extractable Ca (51.7 %) and K (100%) concentrations.

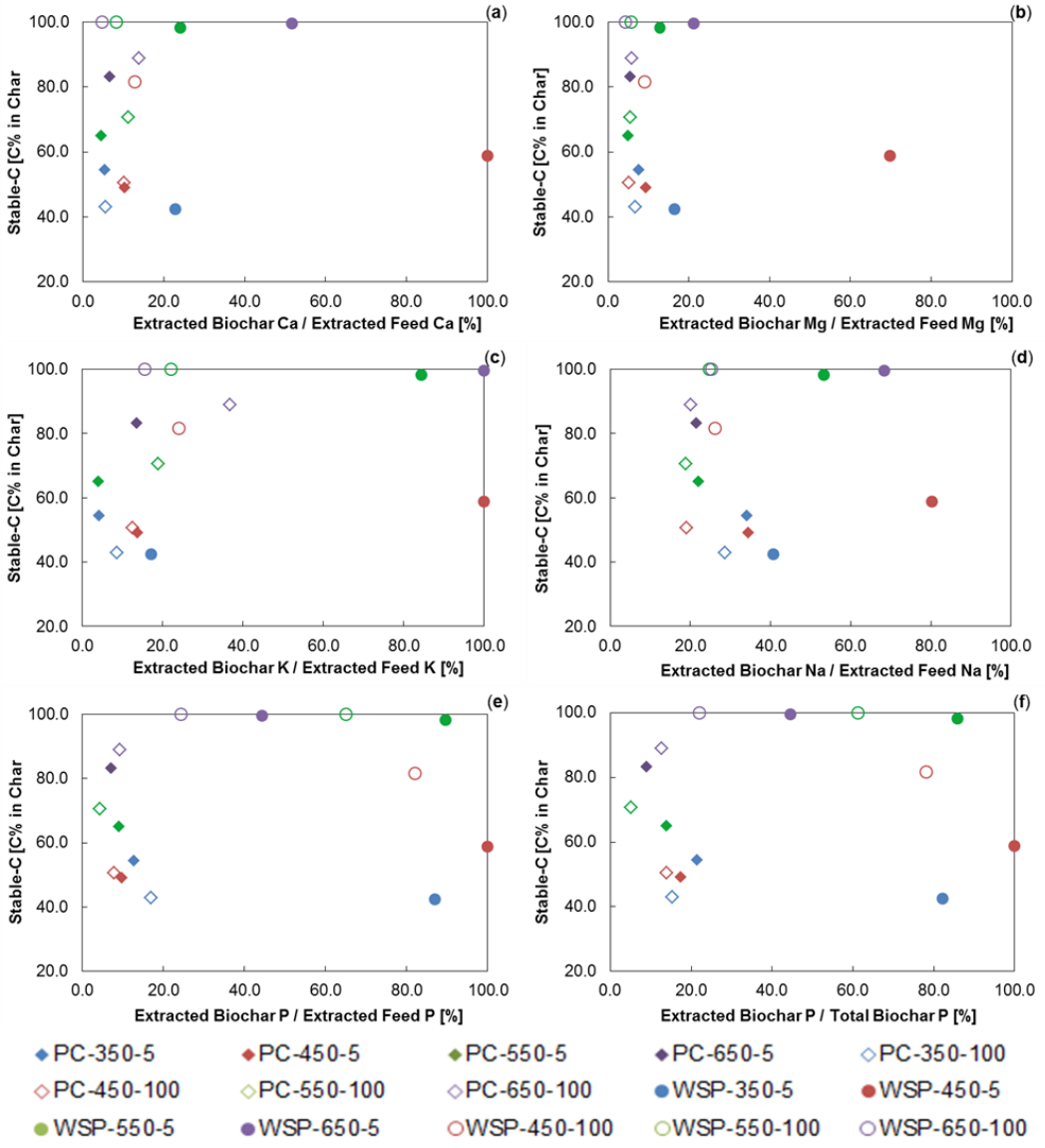

Figure 4-5: Combination of scatter plots showing the comparison of stable-C concentration with the concentration of extractable nutrients, (a) stable-C vs Ca (b) stable-C vs Mg (c) stable-C vs K (d) stable-C vs Na (e) stable-C vs P (f) stable-C vs total P.

When excluding WSP-450-5 (due to low stability), the remaining biochar samples displayed extractable Mg < 22 %, while the majority of Na values fell below 41 %. Due to its content of N, P and K, biochar can serve as a low grade fertilizer (Glaser *et al.*, 2002; Novak & Busscher, 2013) with potential to improve soil quality. Free bases such as K, Ca and Mg can not only increase soil pH but also provide readily available nutrients for plant growth (Glaser *et al.*, 2002; Novak & Busscher, 2013). However, biochar is potentially more important as a soil conditioner and can support nutrient transformation in soil rather than acting purely as a source of nutrients (Glaser *et al.*, 2002). However these nutrient transformations can also result in negative effects on plants, including N deficiency caused by N immobilization (Chan & Xu, 2009; Atkinson *et al.*, 2010) where microorganisms are stimulated by the labile fraction of biochar to decompose available N in soil (NH_4^+ and NO_3^-) or from SOM if the available N concentration in soil is low. A high mineralisation rate has been attributed to a larger labile C fraction present within biochar, making low temperature biochar more likely to cause the activation of soil microorganisms (DeLuca *et al.*, 2009; Nelissen *et al.*, 2012). However the bulk of the remaining organic C present within biochar does not lead to mineralisation-immobilization reactions because of its highly recalcitrant nature (Chan & Xu, 2009). Biochar has also been seen to adsorb NH_4^+ and NH_3^- from soil solution and thus reduce the availability of inorganic N (DeLuca *et al.*, 2009).

4.3.2.3 C stability versus soil enhancement and energy output

The lower stable-C fraction of WSP-450-5 demonstrated that focusing pyrolysis to produce biochar with properties favouring nutrient extraction could affect the C sequestration potential of the related biochar; therefore enhancing both functional properties could prove to be impossible without directly affecting the other property. Although the proportion of extractable nutrients increased between 450^{o}C – 550^{o}C it was actually seen that biochar produced from higher HTT provided the better overall result when combined with the other functional properties of biochar.

Although the energy content of pyrolysis co-products was not covered within this study, previous studies into the energy balance of the system concluded that applying

higher pyrolysis HTTs actually resulted in increased C storage in addition to a larger amount of energy available within liquid and gas products (chapter 5 and 6). When considering the conclusions reported in these studies in conjunction with the results of this work, pyrolysis at HTT $\geq$ 550^{o}C can produce biochar with long-term stability, high alkalinity, high biochar CEC, and deliver good concentrations of nutrients to soil, while providing additional heat and power generation potential through the utilisation of liquid and gas co-products.

4.4 Conclusion

The main objective of this work was to relate differences in biochar functional properties to pyrolysis process parameters, while seeking combinations of functional properties that could lead to improvements to the environmental performance of biochar, hence addressing Objective 1 identified in section 1.7. The results showed that while CEC and concentration of extractable nutrients tended to be more favourable at lower HTTs, high temperature pyrolysis still demonstrated beneficial values for these soil enhancing properties as well as increased alkalinity and stable-C yield. Overall the differences between the functional properties of low and high heating rate biochar were not considerable. The lower heating rate may have produced biochar with marginally more beneficial properties, however the process constraints imposed by slow heating (e.g. low throughput, large equipment) are unfavourable for industrial biochar production. Therefore a combination of production conditions and feedstock under which biochar with positive functional properties of high long-term C sequestration and soil enhancing capabilities was achievable, thus tackling Objectives 3 and 5.

These findings are important and, in conjunction with detailed LCA as well as comparative studies analysing the trade-offs between different benefits i.e. C storage and electricity generation, would provide a firm basis for decisions on best biochar deployment practices. While pyrolysis on a small-scale allowed for the high level of control needed to investigate the impact of production conditions and to identify regions of major property changes, the same control may not be achievable when using industrial-scale pyrolysis. It is reasonable to assume that if biomass particles are exposed to the same thermal history and environment (within the reactor), the same type of biochar can be produced, no matter the scale or type of pyrolysis unit. Therefore the challenge is to design and control the conversion process to ensure the correct processing conditions. Furthermore, field testing of selected biochar is required to first validate laboratory-assessed functions to behaviour in soil, and observe the development of functional properties with time. This work represents an

important first step towards the ambitious goal of bespoke biochar, engineered to deliver a specific environmental response.

Chapter 5. **Studying how production conditions effect the balance between energy generation and carbon sequestration**

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The candidate, as lead author, was solely responsible for all experimentation, laboratory analysis (unless stated otherwise), data analysis and writing of the paper. Co-authors provided guidance and support on the scope and design of the project, the analyses performed and contributed to the editing of the manuscript. Clare Peters and Andrew Cross also provided assistance during stages of the laboratory analysis.

Abstract

This work aimed to investigate the extent to which it is possible to marry the two seemingly opposing concepts of heat and/or power production from biomass with carbon sequestration in the form of biochar. To do this, we investigated the effects of feedstock, HTT, residence time and carrier gas flow rate on the distribution of pyrolysis co-products and their energy content, as well as the C sequestration potential of biochar. Biochar was produced from WP and SP biomass at two temperatures (350^{o}C and 650^{o}C), with three residence times (10, 20 and 40 minutes) and three carrier gas flow rates (0, 0.33 $\pm$ 0.02 and 0.66 $\pm$ 0.02 L min^{-1}). The energy balance of the system was determined experimentally by quantifying the energy contained within pyrolysis co-products. Biochar was also analysed for physicochemical and functional properties, namely environmentally stable-C and labile-C content. Residence time showed no considerable effect on any of the measured properties. Increased HTT resulted in higher concentrations of fixed C, total C and stable-C in biochar, as well as higher HHV due to the increased release of volatile compounds. Increased carrier gas flow rate resulted in decreased biochar yields and reduced biochar stable-C and labile-C content. Pyrolysis at 650^{o}C showed an increased stable-C yield as well as a decreased proportion of energy stored in the biochar fraction but increased stored energy in the liquid and gas co-products. Carrier gas flow rate was also seen to be influential in determining the proportion of energy stored in the gas phase. Understanding the influence of production conditions on long term biochar stability in addition to the energy content of the co-products obtained from pyrolysis is critical for the development of specifically engineered biochar, be it for agricultural use, carbon storage, energy generation or combinations of the three.

5.1 Introduction

With the global production of biomass estimated at >147 billion tons per year, biomass can be regarded as a renewable energy source with the largest potential to contribute to global energy demands (Balat & Ayar, 2005; Bridgwater, 2006; Demirbas, 2007). Biomass has the potential to produce renewable sources of liquid, gaseous and solid fuels while also offering a route for long term carbon storage. The energy contained within biomass can be extracted by different thermo-chemical or biological methods, including fermentation, direct combustion, gasification, pyrolysis etc. During pyrolysis, organic materials decompose to non-condensable gases, condensable organic liquids and a carbonaceous solid material (biochar). As all of these are potentially valuable co-products, biomass pyrolysis is a polygeneration technology, i.e. offers more than one product, and is thus a highly efficient process for biomass conversion (Demirbas, 2007; Chen *et al.*, 2012). Although biochar has high energy content, in many cases its more beneficial application is incorporation into soil to increase the long term storage of carbon, while also providing soil amendment benefits and GHG reduction (Lehmann & Joseph, 2009; Shackley & Sohi, 2010; Sohi *et al.*, 2010).

The liquid product obtained from pyrolysis, known as bio-oil, is a result of rapid and simultaneous depolymerising and fragmentation reactions of the three main components of biomass: cellulose, hemicellulose and lignin. Bio-oil can also be used as a replacement for fossil fuels in boilers, furnaces and, after some treatment and/or engine modifications, in engines for heat and power generation (Boerrigter & Rauch, 2005; Bridgwater, 2012). The composition of bio-oil tends to have a composition which differs greatly from petroleum fuels (Mohan *et al.*, 2006) and contains a high concentration of oxygen (45 – 50 %). Bio-oil consists of two (sometimes three) phases; firstly a non-aqueous phase consisting of insoluble high molecular weight organics (tar) and secondly an aqueous phase containing low molecular weight organo-oxygen compounds (Demirbas, 2007). Bio-oil is a complex mixture of over 300 compounds including acids, aldehydes, ketones, sugars, phenols etc., and can serve as a precursor for synthesis of many other chemicals (Bridgwater, 1996;

Czernik & Bridgwater, 2004; Demirbas, 2007; Balat *et al.*, 2009; Thangalazhy-Gopakumar *et al.*, 2010).

The mixture of non-condensable gases produced during pyrolysis consists mainly of CO_2, CO, CH_4, H_2 and C_2 hydrocarbons. As with the liquid fraction, the gas product can be utilised for heat and power generation in combustion turbines and engines, however the most common application is for providing heat to sustain the pyrolysis process and to dry biomass feedstock (Becidan *et al.*, 2007; Laird *et al.*, 2009; Yoder *et al.*, 2011). The selection of pyrolysis production conditions such as feedstock, moisture content, temperature, heating rate etc. affects the final yield and composition of the gas, liquid and solid products, while also influencing the properties and energy content of these products. The co-production of solid char, liquid bio-oil and pyrolysis gas can improve the efficiency of biomass conversion in different socio-economic contexts, as opposed to a system designed to maximise only one single product (Chen *et al.*, 2012).

Due to the numerous important parameters between different pyrolysis processes (temperature, heating rate, vapour residence time etc.) and the large variety of potentially available biomass for pyrolysis, it is clear that there can be an almost infinite number of different biochar types produced, differing in physicochemical properties and performance for soil amendment (Enders *et al.*, 2012; Ronsse *et al.*, 2013). Maximising the yield of biochar for agricultural application and therefore C sequestration potential has long been associated with decreasing the severity of pyrolysis, resulting in a loss of energy as a result of reduced liquid and gas fractions (Antal & Grønli, 2003; Demirbas, 2004; Demiral & Ayan, 2011; Hossain *et al.*, 2011; Chen *et al.*, 2012; Manyà, 2012; Angin, 2013; Mašek *et al.*, 2013b; Ronsse *et al.*, 2013). Biochar production therefore faces competition for resources from alternative technologies such as fast pyrolysis and gasification which are largely focused on maximising the extraction of energy rich liquid and gas products while generating very small amounts of char (<15%) (Bridgwater, 2012). However, very little is actually known about the influence of production conditions on the product energy distribution and at the same time the C sequestration potential of biochar.

Therefore determining how pyrolysis conditions relate to the functional properties of biochar and energy generation from pyrolysis is pivotal to assessing the potential role of biochar in sequestering C and offsetting C emissions, as well as providing environmental services. Hence this work aims to show the influence that feedstock and production conditions have on the amount of C (both stable and non-stable) and energy stored in biochar, as well as the amount of available energy in pyrolysis liquids and gas (Objectives 1 and 2). This should then lead to an indication into whether and under what circumstances it can be possible to simultaneously achieve high efficiency of biomass conversion to heat and/or power and high C mitigation potential, thus contributing to Objective 3.

5.2 Materials and methods

5.2.1 Feedstock

The two types of biomass used for the pyrolysis experiments were: mixed 5/95 pine:spruce softwood pellets (WP) and mixed 50/50 wheat:oilseed rape straw pellets (SP). All feedstock was used as received with good homogeneity for pellet material. The full details of feedstock particle size, moisture content and supplier can be found in section 2.3.1 in Table 2-1 while the results of ultimate and proximate analysis of the selected materials can also be found in section 2.3.1 in Table 2-2.

5.2.2 Pyrolysis equipment

The experimental set up of the pyrolysis system was described in section 2.3.1 and shown in Figure 2-1.

5.2.3 Pyrolysis conditions

Pyrolysis experiments used a standard mass (100g) for WP and SP, resulting in a different volume of material being used depending on feedstock density. The WP and SP feedstock were selected for investigating the effect of HTT, residence time at HTT and carrier gas flow rate on the energy content of pyrolysis products. Samples of both feedstock types were heated at a rate of $5^{o}C\ min^{-1}$. The WP and SP runs were implemented using HTT of $350^{o}C$ and $650^{o}C$. After pyrolysis, the different products were collected, measured and stored as described in section 2.3.3.

5.2.4 Product Analysis

Detailed descriptions of the analytical procedures carried out during this work can be found in section 2.4. In brief, char samples were analysed using proximate analysis (section 2.4.1.1), ultimate analysis (section 2.4.1.2) and the Edinburgh tool kit for stable-C (section 2.4.2.1.1) and labile-C (section 2.4.2.1.2) concentrations. The heating value was also determined for biochar (section 2.4.3.1), liquid (section 2.4.3.2) and gas products (section 2.4.3.3).

5.3 Results and discussion

It should be noted that where residence time had no statistically significant influence on the properties of interest, an average value was taken for the obtained results to aid in the representation of feedstock, HTT and carrier gas flow rate influence. Presentation of the results in this way may lead to visual exaggeration of trends but statistical analysis was carried out on the entire data set rather than the average values.

5.3.1 Product distribution

The yields obtained for char, liquid and gas products from each pyrolysis experiment are shown in Figure 5-1.

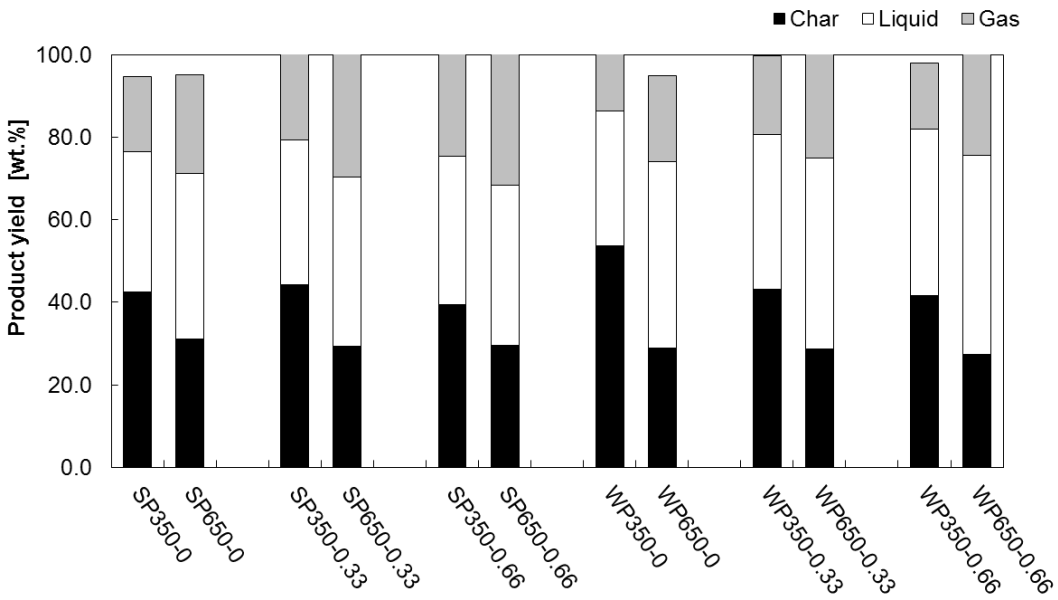

Figure 5-1: Mass distribution of char, liquid and gaseous co-products from slow pyrolysis.

For each feedstock, increasing the pyrolysis HTT from 350^{o}C to 650^{o}C resulted in a decreased char yield and subsequent increase in the yields of liquids and gases. The distribution of the liquid and gas fraction was largely dependent ($P < 0.0001$) on feedstock composition, thus potentially resulting in the varying yields and properties between the two biomass. However, the influence of feedstock on char yield only became significant when in conjunction with HTT ($P < 0.05$). The resulting change

in product yields with temperature is due to increasing decomposition of cellulose, hemicellulose and lignin at elevated HTT causing increased emissions of volatile matter (R^2 = -0.9, P < 0.0001) (Enders *et al.*, 2012; Crombie *et al.*, 2013 (Chapter 3)). WP demonstrated the largest variation between biochar yields as well as the highest (55 %) and lowest (27 %) char yields at 350^{o}C and 650^{o}C respectively. There was a smaller variation observed between SP biochar samples at different HTT. With increasing release of volatile matter, the yields of liquid and gas products could be expected to continue to rise with HTT, however there was a substantially larger increase in the yield of pyrolysis gas compared to that of liquids. This is likely to be due to secondary cracking reactions converting liquid volatiles into gas around 500^{o}C (Chen *et al.*, 2003; Phan *et al.*, 2008; Duman *et al.*, 2011; Fu *et al.*, 2011).

In this work the residence time at HTT had no statistically significant effects on the char, liquid and gas yields (P = 0.23, P = 0.36 and P = 0.79 respectively). Increasing the range of residence times investigated may generate more obvious trends or significant differences in values. However the range used in this study was chosen to correspond to realistic times for biochar production in industrial continuous pyrolysis units.

Reducing the vapour residence time (carrier gas flow rate) could have a direct effect on the composition of liquid and gaseous products obtained from the pyrolysis system by affecting the interactions of the volatile matter with char and other gaseous species. The results in Figure 5-1 show, that although the effect of the carrier gas flow rate on the char, liquid and gas yields (when analysing the full data set) is not as clear as that of temperature, it is still significant (P < 0.05). Pyrolysis of WP in the absence of a carrier gas generated the highest char yields (> 50 %) compared to the other carrier gas flow rates used (< 45 %). As there was no carrier flow, the expelled volatile matter was propelled through the system only by the action of gas produced during pyrolysis. Therefore, these conditions would encourage secondary char formation by interaction of char and volatiles, which could explain the higher char yield and lower liquid and gas yields. When investigating further it was found that carrier gas flow rate had a significant effect on the liquid yields at 350^{o}C however no

impact was observed at 650^{o}C (P = 0.41) potentially due to the maximum liquid yield being reached at ~500^{o}C (Chen *et al.*, 2003; Phan *et al.*, 2008; Duman *et al.*, 2011).

5.3.2 Physicochemical properties

The influence of production conditions on the results obtained from proximate analysis and ultimate analysis is important for quantitative assessment of the composition of biochar as well as an indication of its stability. However, as these results were not the primary focus of this work, only a brief description of the main trends will be provided in the following section.

5.3.2.1 Proximate analysis

Results for proximate analysis of all char samples are shown in Table 5-1. The measured ash content varied greatly between feedstock (P < 0.0001) with higher concentrations found in biochar derived from SP (12 – 23 %) biomass compared to WP biochar (< 3 %). Higher HTT promoted biomass decomposition, leading to higher fixed-C and reduced volatile matter concentrations in the resulting biochar. Similar trends were also exhibited by the corresponding fixed-C and volatile matter yields (feedstock C basis). Carrier gas flow rate and residence time at HTT were both found to have no significant effect (P > 0.05) on the composition of biochar, as determined by proximate analysis.

Table 5-1: Proximate and ultimate analysis for all biochar samples.

	Proximate analysis [wt.% (db)]					Ultimate analysis [wt.% (db)]				
Sample	Fixed C	Volatile Matter	Ash	FC Yield [daf]	VM Yield [daf]	C	H	N	O	C Yield
SP 350-10-0	45.8	39.2	15.0	33.1	28.3	61.4	3.6	1.0	19.0	61.4
SP 350-20-0	45.6	39.1	15.3	33.8	29.0	62.7	4.4	1.1	16.5	62.8
SP 350-40-0	39.5	38.8	21.7	29.3	28.8	56.6	2.9	1.1	17.6	58.0
SP 650-10-0	59.2	19.9	20.9	40.9	13.7	71.1	1.3	1.0	5.8	54.6
SP 650-20-0	57.5	19.6	22.9	39.3	13.4	72.1	1.3	0.9	2.8	52.8
SP 650-40-0	62.9	16.2	20.9	41.6	10.7	73.2	1.2	1.1	3.5	52.4
SP 350-10-0.3	36.7	51.0	12.3	27.6	38.3	55.5	4.2	0.9	27.1	65.9
SP 350-20-0.3	40.0	45.9	14.2	30.3	34.7	60.4	5.2	1.1	19.2	65.0
SP 350-40-0.3	46.8	37.0	16.2	30.8	24.3	62.1	3.0	1.0	17.8	55.1
SP 650-10-0.3	58.3	20.4	21.4	36.5	12.8	69.2	1.2	1.0	7.2	49.3
SP 650-20-0.3	62.2	17.7	20.1	38.8	11.0	71.2	1.0	1.0	6.7	49.9
SP 650-40-0.3	59.3	19.0	21.8	37.0	11.8	71.4	1.1	1.2	4.6	48.8
SP 350-10-0.6	44.2	40.6	15.2	32.0	29.4	62.0	4.7	1.1	16.9	61.4
SP 350-20-0.6	47.1	36.9	16.0	33.1	25.9	62.9	4.6	1.1	15.4	59.0
SP 350-40-0.6	50.4	33.0	16.6	34.7	22.7	64.6	4.3	1.1	13.4	57.3
SP 650-10-0.6	59.4	20.0	20.5	38.1	12.8	71.8	1.6	1.0	5.1	50.9
SP 650-20-0.6	56.1	22.5	21.4	35.8	14.4	68.8	1.4	1.1	7.4	50.2
SP 650-40-0.6	61.8	16.2	22.0	38.3	10.0	72.5	1.3	1.1	3.0	48.4
WP 350-10-0	48.6	50.7	0.8	34.2	35.7	67.3	4.5	0.0	27.5	69.9
WP 350-20-0	50.8	48.0	1.2	33.2	31.4	63.5	5.3	0.1	30.0	64.6
WP 350-40-0	54.5	44.2	1.2	35.6	28.8	68.4	4.6	0.0	25.8	64.4
WP 650-10-0	90.5	8.1	1.4	44.7	4.0	90.4	2.2	0.1	5.9	48.8
WP 650-20-0	90.4	7.5	2.1	43.8	3.6	89.8	2.2	0.1	5.9	47.5
WP 650-40-0	91.3	6.7	2.0	45.1	3.3	90.0	2.0	0.1	5.9	48.5
WP 350-10-0.3	57.9	40.7	1.4	33.4	23.5	71.4	4.5	0.0	22.7	56.9
WP 350-20-0.3	56.4	42.4	1.2	31.8	24.0	70.6	5.5	0.1	22.6	55.8
WP 350-40-0.3	60.2	38.4	1.4	36.1	23.0	71.4	4.5	0.0	22.7	59.1
WP 650-10-0.3	89.0	8.8	2.2	44.9	4.5	92.8	1.7	0.0	3.3	49.3
WP 650-20-0.3	88.5	8.8	2.8	43.2	4.3	87.9	2.1	0.1	7.2	47.5
WP 650-40-0.3	89.4	9.1	1.5	43.1	4.4	90.2	1.8	0.0	6.4	47.5
WP 350-10-0.6	54.6	44.1	1.2	32.4	26.2	70.1	5.1	0.1	23.4	58.6
WP 350-20-0.6	65.7	33.0	1.3	37.3	18.8	76.4	5.0	0.1	17.2	56.1
WP 350-40-0.6	55.9	42.6	1.5	28.7	21.9	67.4	5.9	0.1	25.2	50.6
WP 650-10-0.6	89.0	9.5	1.5	41.7	4.5	90.2	1.8	0.0	6.5	46.2
WP 650-20-0.6	89.2	9.1	1.8	40.1	4.1	87.1	1.8	0.0	9.3	44.2
WP 650-40-0.6	89.1	9.7	1.2	39.8	4.3	87.4	1.8	0.0	9.6	44.1

5.3.2.2 **Ultimate analysis**

Data from ultimate analysis (Table 5-1) showed preferential release of H and O, and retention of C, with increasing HTT for both types of feedstock and all residence times and carrier gas flow rates. As seen with fixed-C, there appeared to be a significant influence ($P < 0.05$) of feedstock on the total biochar C content, with the high ash SP biochar containing a lower amount of C compared to WP biochar at corresponding temperatures. As with fixed-C content, there was no significant effect of the residence time or carrier gas flow rate on C content at either of the two HTTs

used. However as with feedstock selection, the carrier gas flow rate did show an effect on the yield of C (feedstock C basis) obtained at 350°C.

Biochar elemental ratios of O:C and H:C were used to construct a Van Krevelen diagram (Figure 5-2) typically used as a visual representation of the age/maturity and origin of hydrocarbon materials such as coal and petroleum. There was a distinct separation between low and high temperature biochar with 650°C char being classified as highly stable according to criteria proposed by Spokas (2010), IBI biochar guidelines (IBI, 2013) and European biochar guidelines (Schmidt *et al.*, 2012). At 650°C all biochar samples contained O:C ratio of < 0.08 indicating high stability while the spread of O:C values for 350°C ranged from 0.16 – 0.37 for SP and 0.17 – 0.36 for WP.

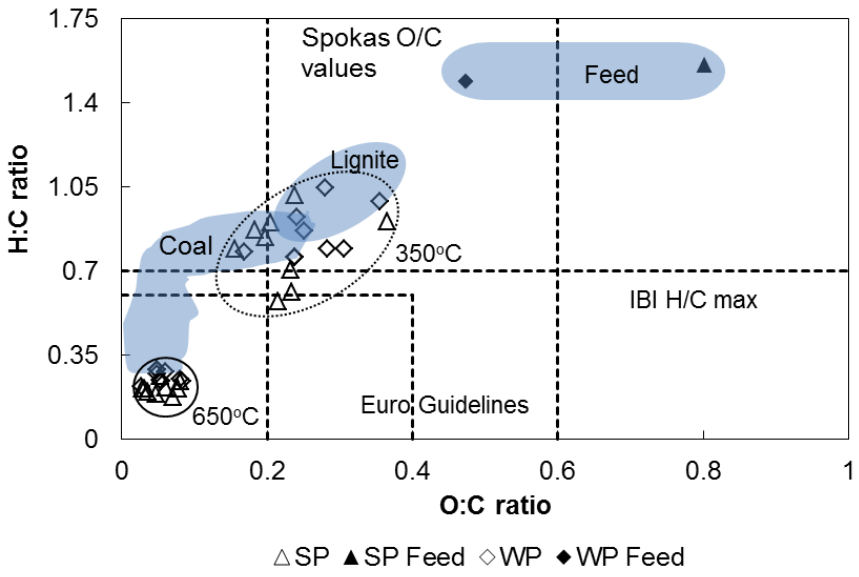

Figure 5-2: Van Krevelen diagram indicating the stability of SP and WP biochar.

5.3.3 Biochar functional properties

The following section will present the results of two analytical tools, developed to assess the carbon storage potential of biochar. Residence times used at both HTT had no significant influence (P > 0.6) on the stable-C and labile-C content of biochar and therefore won't be discussed further, although the data will be used in place of

replicates to examine effects of other parameters. The error bars used in Figure 5-3 and Figure 5-4 represent the three replicates done at the same HTT and carrier gas flow rate, but different holding time.

5.3.3.1 Carbon stability

Results for stable-C content (on biochar C basis) and stable-C yield (on feedstock C basis), determined by the direct oxidation method, are plotted in Figure 5-3.

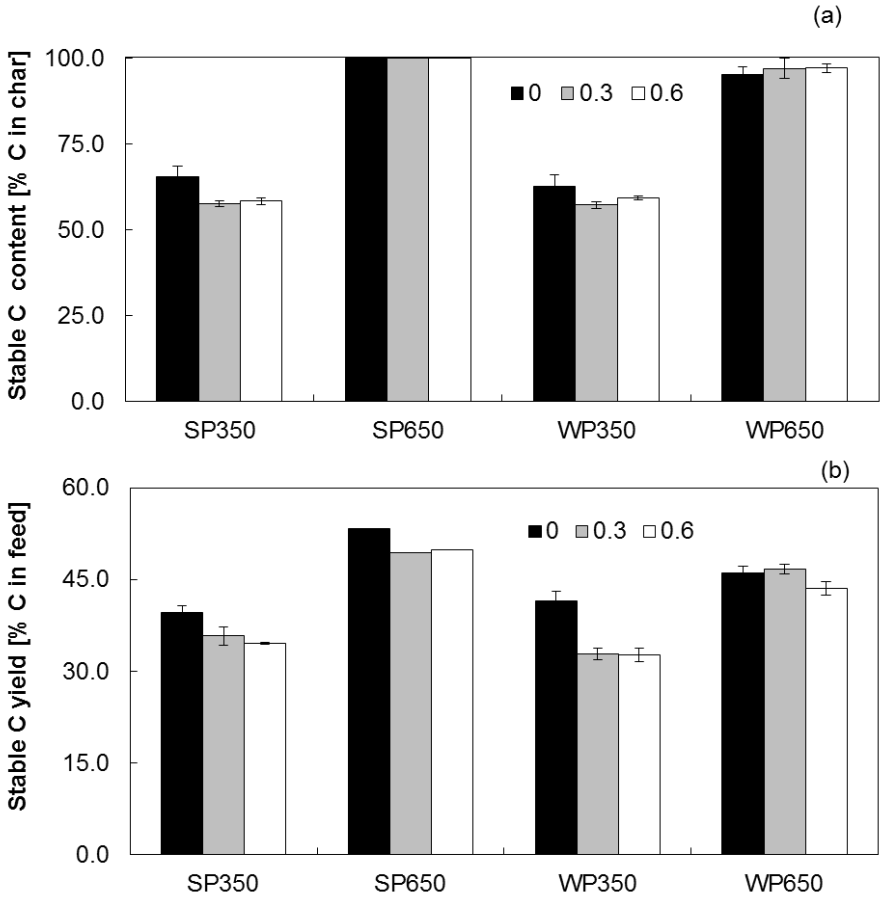

Figure 5-3: Environmental stability of SP and WP char expressed on (a) char C basis (b) feedstock C basis.

It can be seen that HTT was the main factor influencing the concentration and yield of stable-C, agreeing with trends seen in Chapters 3 and 4, with higher HTT resulting in much higher biochar stability ($P < 0.0001$) and a higher proportion of feedstock C

being locked in the form of a stable biochar carbon. The stable-C content range at 350^{o}C was 57 – 65 % while a HTT of 650^{o}C raised these values to 95 – 100 %.

Besides the HTT, the carrier gas (N_2) flow rate also had an important effect on stable-C content and yield. With decreasing carrier gas flow rate the stability and yield of stable-C increased, especially at low HTT. This can be explained by devolatilisation of char particles, resulting in enhanced formation of secondary char within and on the surface of biochar. Although the effect of carrier gas flow rate was only secondary to that of HTT, our results show that it is an important parameter influencing biochar yield and properties. On the other hand, feedstock showed only minimal if any effect ($P > 0.05$) on the stable-C content of chars produced at low HTT (350^{o}C) and slight, but statistically significant ($P < 0.05$) effect at high HTT (650^{o}C). Expressing results on a feedstock C basis (stable-C yield) provides a useful way of assessing the efficiency of feedstock C conversion to stable-C that can be sequestered in the form of biochar. Results in Figure 5-3 show that although the biochar yield (wt. %) was greatly reduced as HTT was increased there was still an overall increase in stable-C yield from 350^{o}C to 650^{o}C. This observation was in accordance with results presented in Chapter 3 and Chapter 4 for different feedstock further iterating the added benefit of stored C at elevated HTT.

5.3.3.2 **Labile carbon**

The content of labile carbon, defined as carbon readily accessible to soil microbes, is mainly affected by the HTT and feedstock, as shown in Figure 5-4. With increasing HTT from 350°C to 650°C, the content of labile-C in biochar dropped dramatically to levels below 0.1 wt.%. Feedstock type was also shown to be an important factor in determining labile-C content, at least at low HTT. Pyrolysis of SP at 350^{o}C resulted in char with much higher labile-C content (1.86 $\pm$ 0.29 %) than that produced by pyrolysis of WP (0.15 $\pm$ 0.05 %). This further demonstrates the trend seen in Chapter 4 of straw biochar containing higher concentrations of labile-C compared to woody biochar. The influence of feedstock decreased with pyrolysis HTT, resulting in no significant effect ($P > 0.05$) at 650^{o}C due to the dominant impact of temperature. The

carrier gas flow rate was also found to have no significant effect ($P > 0.65$) on the final labile-C content or labile-C yield obtained at either HTT (Figure 5-4).

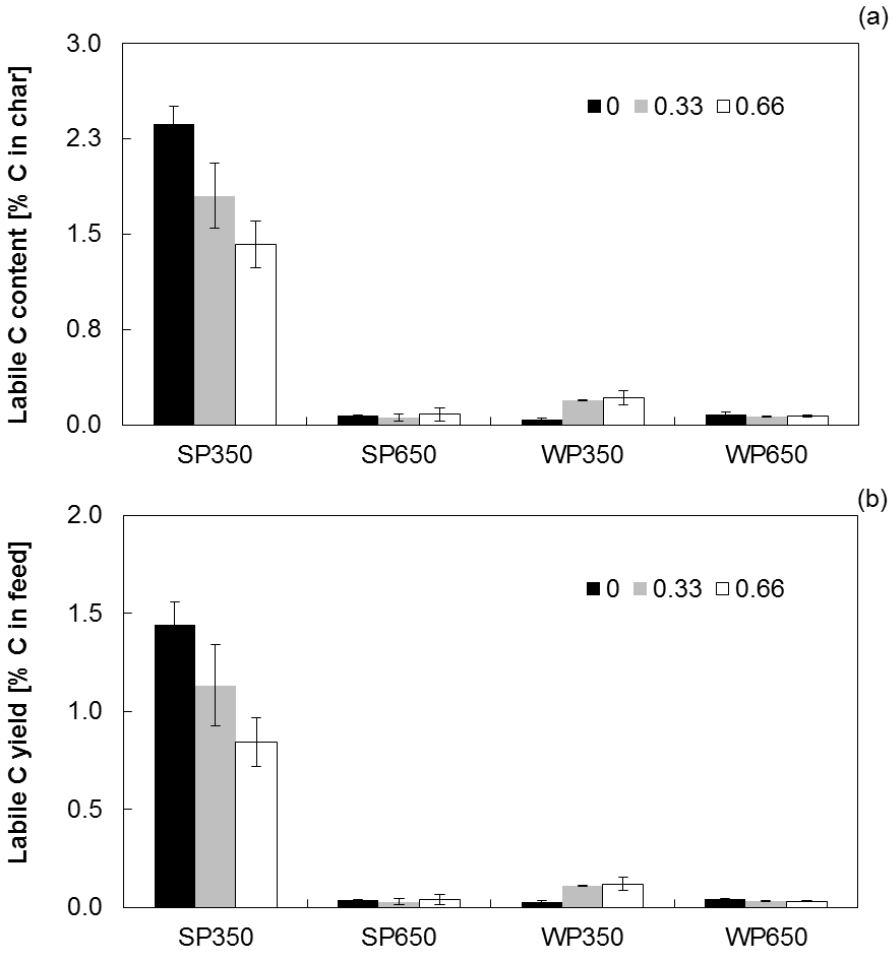

Figure 5-4: Labile-C content of SP and WP biochar expressed on (a) char carbon basis (b) feedstock carbon basis).

5.3.4 Heating value of pyrolysis co-products

The HHV data for solid, liquid and gas products obtained from each experiment are presented in Table 5-2. The following section discusses the relative distribution of energy among the three co-products of slow pyrolysis and how it is affected by the process conditions.

The HHV for each biochar sample was seen to increase with increasing HTT with a larger difference occurring for WP biochar. This is due to the fact that with

increasing pyrolysis severity the char composition shifts closer towards pure carbon with HHV of 32.8 MJ kg^{-1} (Ronsse *et al.*, 2013). Ronsse *et al.* (2013) also suggested that the presence of ash in the char can lead to a 'dilution' of the energy content resulting in lower than pure carbon HHV for fully carbonized materials. The lower HHV for SP chars produced at 650^{o}C could be explained by this 'dilution' effect as a result of the increasing ash concentration with temperature and the higher ash content of SP chars compared to WP. Alternatively, the presence of C-H, C-O and O-H bonds remaining in the char have been seen to influence the HHV of biochar; in particular wood derived biochar has been shown to produce HHV higher than pure carbon (up to 35 MJ kg^{-1}) (Ronsse *et al.*, 2013). However the HHV of wood materials may in fact peak and then decline as the heterogeneous bonding is sequentially decreased following stabilization of the carbon structure (Ronsse *et al.*, 2013). Temperature clearly had the largest influence ($P < 0.0001$) on the char HHV with carrier gas flow rate ($P = 0.003$) and feedstock ($P < 0.0001$) also having a significant impact. However, the effect of carrier gas flow rate on the char heating value was only observed at 350^{o}C with no effect seen at 650^{o}C ($P > 0.05$). The observed trend of biochar HHV can then be used to further emphasize the dominance of temperature on biochar properties at 650^{o}C. Residence time had no significant influence ($P > 0.75$) on the HHV of biochar at either HTT.

The HHV for the liquid samples produced during each experimental run were unaffected by increases in HTT, residence time and carrier gas flow rate ($P > 0.5$). Therefore the difference in liquid HHV was mainly derived from feedstock composition ($P = 0.002$) with the average liquid heating values for SP and WP measured as 7.24 $\pm$ 0.2 MJ kg^{-1} and 6.20 $\pm$ 0.21 MJ kg^{-1} respectively. Biochar ash concentration and HHV of liquids did show a moderate correlation ($R^2 = 0.46$, $P = 0.005$) indicating the small difference between SP and WP liquid HHV could be related to the increased ash concentration of SP biomass. The HHV of pyrolysis gas was calculated based on the gas composition as shown in Figure 5-5.

Table 5-2: HHV for solid, liquid and gas co-products obtained from slow pyrolysis.

Higher Heating Value of Pyrolysis Co-Products						
Sample	Char HHV [MJ/kg]	Liquid HHV [MJ/kg]	Gas HHV [MJ/kg]	Energy contained in Char [MJ]	Energy contained in Liquid [MJ]	Energy contained in Gas [MJ]
SP 350-10-0	24.1	7.8	3.2	10.1	2.7	0.5
SP 350-20-0	23.1	7.1	3.2	9.7	2.5	0.6
SP 350-40-0	23.8	7.4	3.3	10.3	2.4	0.6
SP 650-10-0	24.0	7.2	9.7	7.7	2.9	2.0
SP 650-20-0	23.0	8.2	9.7	7.1	3.2	2.7
SP 650-40-0	24.4	6.2	11.1	7.3	2.5	2.5
SP 350-10-0.3	21.6	6.4	2.5	10.8	2.0	0.5
SP 350-20-0.3	22.1	8.2	2.8	10.0	2.8	0.7
SP 350-40-0.3	22.3	9.2	3.5	8.3	3.7	0.9
SP 650-10-0.3	24.7	7.3	9.4	7.4	3.0	3.0
SP 650-20-0.3	25.1	6.9	9.5	7.4	2.8	3.0
SP 650-40-0.3	23.5	6.3	7.8	6.8	2.6	2.5
SP 350-10-0.6	24.6	6.3	3.9	10.2	2.1	1.0
SP 350-20-0.6	24.6	7.1	4.3	9.7	2.6	1.1
SP 350-40-0.6	24.3	6.4	4.7	9.1	2.4	1.3
SP 650-10-0.6	24.8	7.1	9.4	7.4	2.8	3.3
SP 650-20-0.6	24.1	7.2	9.3	7.4	2.8	3.0
SP 650-40-0.6	25.9	8.3	9.8	7.2	3.2	3.6
WP 350-10-0	27.7	5.3	2.3	15.5	1.7	0.3
WP 350-20-0	26.7	8.2	2.0	14.6	2.8	0.3
WP 350-40-0	27.6	5.6	2.1	13.9	1.8	0.3
WP 650-10-0	33.6	6.6	9.8	9.7	2.9	2.1
WP 650-20-0	33.6	5.7	8.9	9.6	2.7	1.9
WP 650-40-0	33.9	6.8	10.6	9.8	3.0	2.1
WP 350-10-0.3	27.6	6.5	3.1	11.8	2.5	0.6
WP 350-20-0.3	27.8	6.4	3.0	11.8	2.4	0.6
WP 350-40-0.3	27.1	6.2	3.3	12.0	2.3	0.6
WP 650-10-0.3	33.3	5.2	6.0	9.5	2.4	1.7
WP 650-20-0.3	33.2	4.8	8.1	9.6	2.2	2.0
WP 650-40-0.3	33.1	6.5	8.0	9.4	3.0	2.0
WP 350-10-0.6	27.7	6.1	4.8	12.5	2.3	0.8
WP 350-20-0.6	28.7	4.6	5.1	11.3	1.9	0.8
WP 350-40-0.6	28.9	6.6	4.5	11.7	2.8	0.7
WP 650-10-0.6	33.7	6.1	11.4	9.3	2.9	2.8
WP 650-20-0.6	33.7	7.4	12.2	9.2	3.6	3.1
WP 650-40-0.6	33.4	6.9	12.8	9.1	3.3	3.4

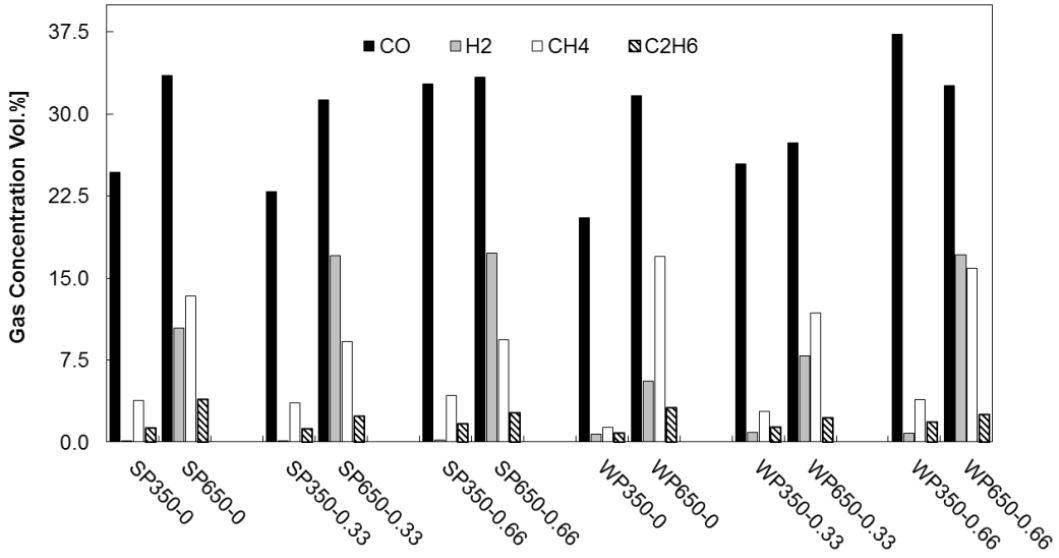

Figure 5-5: Effect of temperature and carrier gas flow rate on the gas composition.

It can be seen that the pyrolysis gas HHV increases considerably with increasing HTT, as a result of increased concentrations of H_2, CH_4, C_2H_6 and CO measured in the pyrolysis gas. The increase in these species could be a result of aromatic condensation and secondary thermal cracking of heavy hydrocarbons occurring above 550^{o}C (Chen *et al.*, 2003, 2012; Mohan *et al.*, 2006; Yang *et al.*, 2006a; Duman *et al.*, 2011; Fu *et al.*, 2011). The release of CO_2 and CO is predominantly associated with the cracking and reforming of carbonyl, ether groups and thermolabile carboxyl, while CO can also be formed through the secondary decomposition of volatiles at higher temperatures (Yang *et al.*, 2006a; Fu *et al.*, 2011). The cracking and reforming of aromatic rings has been described as a pathway for the formation of H_2, as well as the formation of CH_4 through the rupture of methylene groups (Chen *et al.*, 2003; Yang *et al.*, 2006a; Wang *et al.*, 2009; Fu *et al.*, 2011). Feedstock and residence time were deemed to have no influence ($P > 0.45$) on the pyrolysis gas HHV, while carrier gas flow rate had a significant effect ($P < 0.0001$). Concentrations of H_2, CH_4 and C_2H_6 increased with a higher carrier gas flow rate resulting in increased pyrolysis gas HHV. The resulting increase in HHV was also generated by diminishing CO_2 content with HTT and carrier gas flow rate. This was probably due to the decreased vapor residence time allowing for energy

rich species to be swept away from hot char surfaces minimizing secondary reactions.

Biochar has a high energy content and therefore can be an attractive source of heat for powering the pyrolysis process especially in systems where biochar is not the desired product (i.e. fast pyrolysis and gasification) (Yoder *et al.*, 2011; Bridgwater, 2012). However, under certain production conditions the energy contained within the gas stream could be sufficient to achieve the energy input requirements of a pyrolysis system thus leaving the biochar product available for soil enhancing and C storing applications. The effect of production conditions on the gas heating value and therefore its potential to power a pyrolysis system were studied further in Chapter 6.

5.3.5 Energy distribution among co-products

The contribution of each co-product to the overall energy balance was determined by expressing the co-product energy content as a proportion of the feedstock energy content. There was no considerable effect of residence time on the energy distribution among the different product fractions so an average of the values for the different residence times was calculated to demonstrate the influence of HTT and carrier gas flow rate on the energy balance (Figure 5-6).

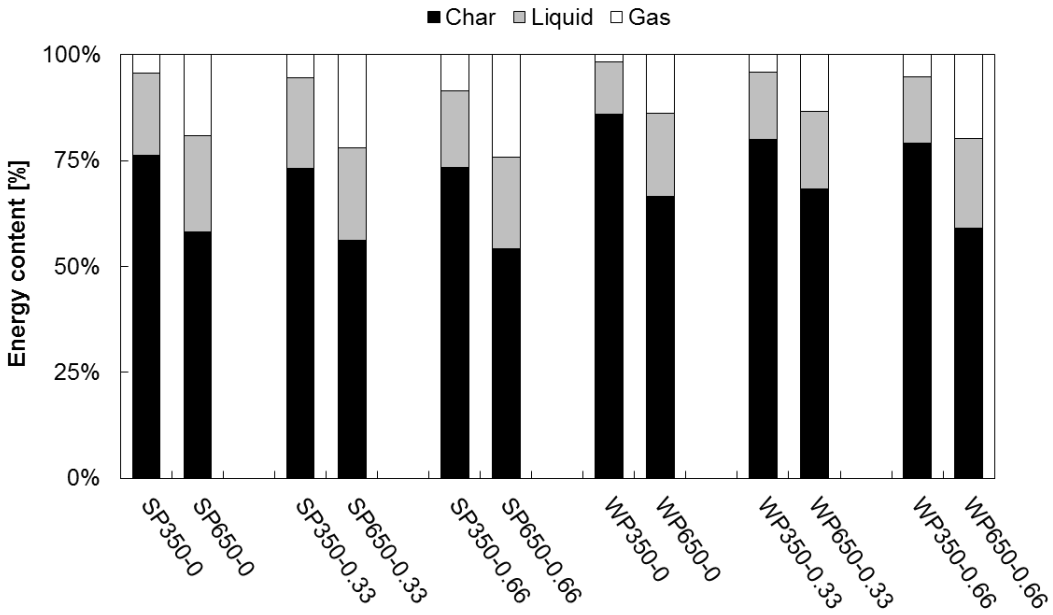

Figure 5-6: Normalised energy content distribution among char, liquid and gas co-products.

As the HTT was increased, biochar showed a significant ($P < 0.0001$) decrease in its contribution to the total energy balance of 15.8 $\pm$ 0.47 % for SP and 18.9 $\pm$ 6.57 % for WP material (Figure 5-6). The degree of reduction in the biochar contribution was smaller for SP biochar samples, perhaps due to dilution effect of ash content on biochar HHV. The HHV of the individual liquid samples did not show an increase with HTT but the overall liquid yield and therefore liquid contribution to total energy balance did ($P = 0.003$). Increasing the HTT from 350^{o}C to 650^{o}C increased the liquid contribution to total energy from 2.43 $\pm$ 0.26 MJ kg^{-1} to 2.88 $\pm$ 0.19 MJ kg^{-1}, which represents 2.56 % and 2.85 % of the total energy recovered in pyrolysis co-products for WP and SP respectively. The contribution of the pyrolysis gas to the total energy balance showed a significant ($P < 0.0001$) increase with higher HTT, due to increased gas yield, as well as substantially higher gas HHV at 650^{o}C. Similarly, increasing the carrier gas flow rate also resulted in a significant increase ($P < 0.0001$) in the gas energy contribution to total energy balance, as a result of higher gas yields obtained at higher carrier gas flow rates. Overall, HTT was the controlling variable in determining the distribution of the total energy among the solid, liquid

and gas co-products; however carrier gas flow rate and feedstock were also determining factors at the lower HTT.

5.3.6 **Carbon emissions**

A breakdown of the C mass distribution between the char, liquid and gas fractions was shown in Table 5-3. With rising HTT, an increasing amount of C is apportioned to the liquid and gas fractions, at the expense of C in the char. However, as previously shown in Figure 5-3 and Chapter 3 and Chapter 4, despite a decreasing char C content with rising HTT, the biochar stable-C yield increases and therefore the mass of stable-C also increases. It is important to note that the stability of stable-C (> 100 years) and relatively non-stable labile-C (two week incubations) do not account for the total C present in the char, indicating a third fraction of intermediate stability. This additional C fraction (Int-C) can be considered to have intermediate stability (2 weeks < Int-C < 100 years), as it could be rapidly released over a number of years or equally remain stable for decades. Therefore two values for total mass of emitted C can be calculated for each set of pyrolysis conditions i) intermediate C considered to be stable and therefore not included in calculation of emitted C ii) intermediate C considered to be unstable and therefore included in calculation of emitted C.

Table 5-3: Distribution of carbon among co-products.

	C in char [g]			C in co-products [g]		Stored C [g]		Emitted C [g]	
Sample	Stable-C	Labile-C	Int -C	C in liquid	C in Gas	With Int-C	W/O Int-C	W/O Int-C	With Int-C
SP350-0	15.5	0.6	7.7	10.1	5.3	23.2	15.5	15.9	23.6
SP650-0	21.1	0	0	10	8.6	21.1	20	18.5	18.5
SP350-0.33	14.2	0.5	10	8	7.1	24.2	14.2	15.5	25.5
SP650-0.33	20.1	0	0	9.8	10.9	20.1	19.1	20.7	20.7
SP350-0.66	13.9	0.3	9.5	8.2	8.2	23.4	13.9	16.7	26.2
SP650-0.66	19.8	0	0	8.1	11.8	19.8	18.8	19.9	19.9
WP350-0	20	0	11.9	12.5	3.7	31.9	20	16.2	28.2
WP650-0	22.3	0	1.1	18.1	7	23.4	22.3	25.1	26.2
WP350-0.33	16	0.1	11.9	15.5	5.3	27.9	16	20.9	32.8
WP650-0.33	22.8	0	0.7	17.1	8.3	23.5	22.8	25.3	26
WP350-0.66	16.1	0.1	11	17.2	4.9	27.1	16.1	22.2	33.2
WP650-0.66	21.5	0	0.6	19.9	7.3	22.1	21.5	27.2	27.8

The significance of the Int-C is much larger at low pyrolysis temperatures, so much so that pyrolysis at 350^{o}C actually released a higher amount of C per MJ of chemical energy produced than at 650^{o}C, when the Int-C is deemed to be emitted rather than stored (Figure 5-7).

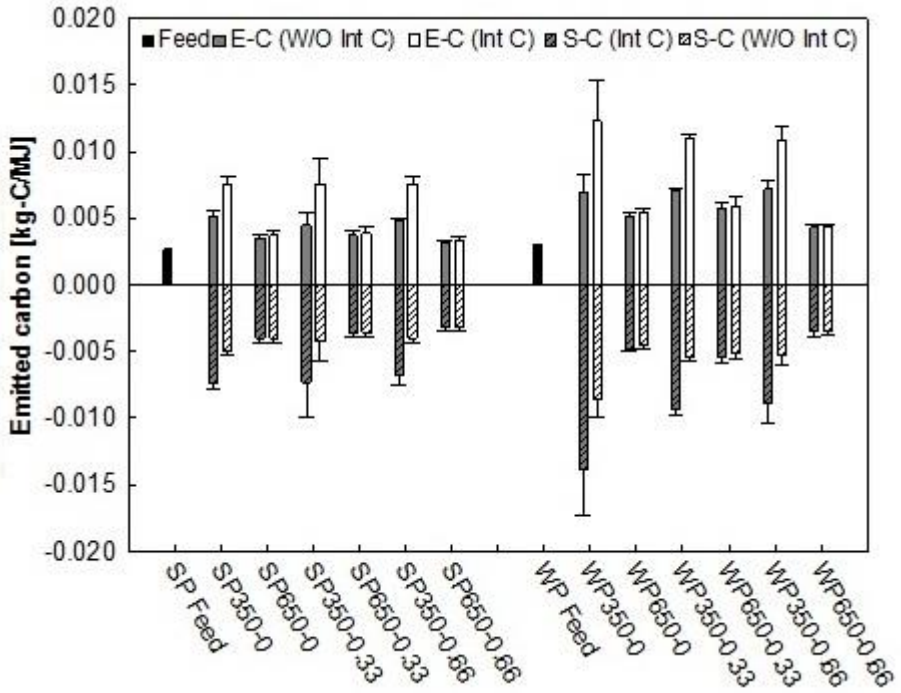

Figure 5-7: The effect of HTT and carrier gas flow rate on the amount of stored and emitted C per MJ of chemical energy produced from slow pyrolysis.

There is little to no difference of the Int-C fraction on the amount of C being emitted per MJ of chemical energy produced at higher pyrolysis temperatures due to the majority of remaining biochar C being highly stable. When compared to direct combustion of the biomass feedstock, all pyrolysis experiments produced higher relative emissions. However the relative emissions for SP at 650^{o}C were not hugely different to those for biomass combustion, and were considerably lower when the carbon stored in biochar was accounted for. This analysis is subject to a number of limitations; firstly, it works with theoretically available energy in the different material streams, and does not take into account conversion efficiencies of processes potentially utilising these fuels. Secondly, it does not include consideration of direct

and indirect impacts of biochar on GHG emissions when used in agriculture. These additional benefits can play an important role in overall system-wide carbon balance, and should be included in an LCA, based on the results of this work.

5.4 Conclusion

Biochar production competes for resources with more established technologies such as fast pyrolysis and gasification that are tuned for electricity or liquid biofuels production and are therefore often heavily subsidized. This focus of utilizing organic feedstock for energy rather than soil amendment or C abatement has led to literature dominated by reports on the composition and heating values of fast pyrolysis products, with only a relatively limited number of publications focusing on slow pyrolysis. Therefore there are gaps in the knowledge needed to fully assess biochar pyrolysis systems and their potential contribution to GHG management and renewable energy production (Angin, 2013; Gronnow *et al.*, 2013; Jeffery *et al.*, 2013; Ronsse *et al.*, 2013; Troy *et al.*, 2013).

The results of this chapter showed that increasing the severity of pyrolysis raised the HHV of the co-products; however these values on their own do not provide a complete picture of the distribution of energy among co-products. By combining the product yields and product HHV, the energy distribution between co-products and their resulting heat/power production potential could be evaluated, while also assessing any consequential loss of C sequestration potential. It is important to note that the calculated energy balance was based solely on the individual HHV of the collected products and their yields. No additional consideration of the energy input needed to reach the different temperatures and associated losses was made, as these are very much process/equipment dependent, and thus presents a first approximation, and important basis for more detailed case studies with detailed LCA, e.g. along the lines of Laird *et al.* (2009) and Shackley *et al.* (2011).

Overall, HTT was the controlling variable in determining the distribution of the total energy content among the solid, liquid and gas co-products, however carrier gas flow rate and feedstock were also determining factors at the lower HTT. Increasing the severity of pyrolysis resulted in a lower contribution of biochar to the overall energy balance, thus reducing the energy potentially lost due to application of biochar to soil. Consequently, the higher HTT increased the energy contained in liquid and gas

products which could be associated with increased emissions from the combustion of these products for heat/power production. In the case of pyrolysis at HTT of 350^{o}C, most of the energy is contained in the char, and therefore unavailable for heat/power generation, while at 650^{o}C, most energy is contained in the liquid and gaseous streams. As a result, low temperature pyrolysis releases more C per MJ of chemical energy compared to pyrolysis at 650^{o}C. Hence pyrolysis at higher temperatures actually produces fewer emissions per MJ of chemical energy available in the liquid and gaseous co-products, while also securing a larger fraction of C in a stable biochar form.

Therefore, increasing the severity of pyrolysis, at least within the limits investigated, increased the energy value of the pyrolysis co-products, without sacrificing the C storage potential of biochar, therefore addressing Objective 2. These findings in conjunction with those presented in Chapter 3 and Chapter 4 present an important step towards realising the potential for producing a biochar product with important functional properties, while at the same time improve the energy output of the system.

Chapter 6. **Investigating the potential for a self-sustaining slow pyrolysis system under varying production conditions**

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The candidate, as lead author, was solely responsible for all experimentation, laboratory analysis (unless stated otherwise), data analysis and writing of the paper. The co-author provided guidance and support on the scope and design of the project, the analyses performed, and contributed to the editing of the manuscript.

Abstract

This work aimed to investigate the impact of HTT, heating rate, carrier gas flow rate and feedstock on the composition and energy content of pyrolysis gas to assess whether a self-sustained system could be achieved through the combustion of the gas fraction alone. This would then leave other co-products available for alternative high-value uses. Calculations based on gas composition showed that the pyrolysis process could be sustained by the energy contained within the pyrolysis gases alone. The lower energy limit (6 % biomass HHV) was surpassed by pyrolysis at $\geq 450^{o}C$ while only applying a HTT of $650^{o}C$ consistently met the upper energy limit (15% biomass HHV). These findings fill an important gap in open literature related to the energy balance of the pyrolysis systems for biochar production, and show that, at least from an energy balance perspective, self-sustained slow pyrolysis for co-production of biochar and liquid products is feasible.

6.1 Introduction

Out of the three pyrolysis co-products, biochar (HHV ~18 MJ kg^{-1}) and bio-oil (HHV ~17 MJ kg^{-1}) can be regarded as medium to high-energy-density materials, while pyrolysis gas (HHV ~6 MJ kg^{-1}) (Bridgwater, 2006; Laird *et al.*, 2009) is a low-energy-density product. Besides their use as solid and liquid biofuels, biochar and bio-oil have a host of alternative high value applications which could considerably improve the economic viability of the pyrolysis system. Extraction of high-value chemicals from pyrolysis liquids (bio-oil) and/or their upgrading to liquid biofuels is a promising route to efficient decarbonisation of the transport and chemical industry (Czernik & Bridgwater, 2004; Bridgwater, 2012). Such chemical products can provide comparable revenue to fuel and energy products even with such relatively small amounts (around 5 %) used for this purpose, making for an attractive alternative use for bio-oil (Czernik & Bridgwater, 2004; Bridgwater, 2012). In addition to bio-oils' added benefits, biochar can also offer numerous environmental and agricultural benefits such as improved soil fertility and long-term storage of C in the environment (Lehmann, 2007; Lehmann *et al.*, 2009; Woolf *et al.*, 2010). This is achieved through the highly recalcitrant nature of biochar as well as its ability to influence nutrient retention, water holding capacity, soil pH, CEC and reducing or supressing the emission of GHG such as CO_2, N_2O and CH_4 (Lehmann, 2007; Chan & Xu, 2009; Manyà, 2012). Woolf *et al.* (2010) described how the C mitigation impact of biochar is about 25% larger, on average, than the impact obtained if the same biomass was fully combusted for energy. Therefore, the incorporation of biochar into soils to provide soil amendment benefits, reduced environmental pollution as well as long term C sequestration may, in many cases, be the preferred alternative to combustion (Lehmann, 2007; Lehmann *et al.*, 2009; Manyà, 2012; Sohi, 2012).

Due to its typically low heating value, pyrolysis gas is potentially better suited for heating of the unit or feedstock drying than for power generation (Becidan *et al.*, 2007; Chen *et al.*, 2012). The mixture of non-condensable gases produced during pyrolysis consists of a number of combustible gases, e.g., CO, CH_4, H_2 and C_2-

hydrocarbons but also a high concentration of incombustible CO_2. These gases are produced during pyrolysis due to thermally favoured reactions such as depolymerisation, decarboxylation, demethanation etc. (González *et al.*, 2003; Duman *et al.*, 2011; Fu *et al.*, 2011), and the processes are relatively well understood. However, there are only a few studies focused on the composition and application of gases released during slow pyrolysis (Williams & Besler, 1996; Duman *et al.*, 2011; Fu *et al.*, 2011; Chen *et al.*, 2012). Several studies have attempted to assess the energy required for pyrolysis as a fraction of the feedstock calorific value (Daugaard & Brown, 2003; Bridgwater, 2006; Gronnow *et al.*, 2013; Yang *et al.*, 2013), however these studies have not considered how varying production conditions during slow pyrolysis may influence the final energy distribution among pyrolysis co-products. Therefore, there is a gap in understanding of the energy balance of biochar production, which has been reflected in LCA studies to date.

To address this gap, the work reported here focused on investigating the influence that feedstock, HTT, heating rate and carrier gas flow rate have on the composition and related energy content of pyrolysis gases (Objective 2). The energy content of the pyrolysis gas was then used to assess the extent to which pyrolysis gases alone could sustain a pyrolysis process. To our knowledge no literature currently exists which has attempted to investigate the impact of this combination of production conditions on the yield and composition of slow pyrolysis gas in one study. Therefore an alternative source of fuel to run the pyrolysis system could free up the solid and liquid co-products of pyrolysis to be used for higher-value applications, e.g. transportation fuels, bio-chemicals and biochar for environmental and soil applications, to maximise the energy and agricultural benefits of the entire system (Objective 3 and 5).

6.2 Materials and methods

As the pyrolysis gas composition (and therefore heating value) was the main focus of this chapter all information retaining to the production and analysis of the respective biochar fractions can be found in Chapter 4 (PC, WS and WSP biochar) and Chapter 5 (SP and WP biochar).

6.2.1 Pyrolysis equipment

The experimental set up of the pyrolysis system was described in section 2.3.1 and shown in Figure 2-1.

6.2.2 Pyrolysis conditions

Pyrolysis gas was collected during all pyrolysis experiments carried out in Chapter 4 and 5. Chapter 4 (PC, WS and WSP) studied the effect of HTT, heating rate and feedstock on gas composition while Chapter 5 (WP and SP) investigated the influence of residence time and carrier gas flow rate in addition to also studying HTT and feedstock selection. Chapter 4 applied four HTTs (350^{o}C, 450^{o}C, 550^{o}C and 650^{o}C) and two heating rates (5^{o}C min^{-1} and 100^{o}C min^{-1}) while Chapter 5 used two HTTs (350^{o}C and 650^{o}C), three residence times (10, 20 and 40min) and three carrier gas flow rates (0, 0.33 $\pm$ 0.02 and 0.66 $\pm$ 0.02 L min^{-1}).

6.2.3 Product analysis

6.2.3.1 Gas analysis

Gas samples were collected and analysed for gas HHV/LHV and CGE as described in section 2.4.3.3.

6.3 Results and discussion

6.3.1 Influence of pyrolysis conditions on gas composition

The results for gas HHV/LHV and CGE as well as the energy content of pyrolysis gas for each pyrolysis experiment was shown in Table 6-1.

6.3.1.1 Highest treatment temperature

The composition and yields of pyrolysis co-products are a result of the thermal decomposition of key biomass constituents, such as cellulose, hemicellulose and lignin. The composition of these components and the temperature regions over which they decompose ultimately determine the gas composition obtained during pyrolysis (Williams & Besler, 1996; Di Blasi *et al.*, 1999; Mohan *et al.*, 2006). Hemicellulose has been shown to decompose between 200^{o}C and 375^{o}C, leading mainly to the release of CO and CO_2, while cellulose decomposes at slightly higher temperatures between 250^{o}C and 380^{o}C, leading to additional release of CO, CO_2 and small amounts of CH_4. Lastly lignin gradually decomposes over a wide temperature range (180^{o}C – 550^{o}C) predominately leading to the release of H_2, CH_4 and C_2 hydrocarbons (González *et al.*, 2003; Mohan *et al.*, 2006; Becidan *et al.*, 2007; Duman *et al.*, 2011; Chen *et al.*, 2012). While the decomposition of these biomass constituents is largely responsible for the variation in gas composition up to approximately 500^{o}C, above this HTT the secondary cracking of vapours becomes the dominant mechanism influencing the gas composition (González *et al.*, 2003; Yang *et al.*, 2006b; Becidan *et al.*, 2007; Chen *et al.*, 2012).

Table 6-1: Influence of production conditions on the energy content of pyrolysis gas to determine the self-sustaining potential of the pyrolysis system.

Self-Sustainable Pyrolysis							
				Energy Limit		Cold Gas Efficiency	
Sample	Gas HHV* [MJ/kg]	Gas LHV* [MJ/kg]	Gas Energy Content† [MJ/kg]	Lower Limit [MJ/kg]	Upper Limit [MJ/kg]	HHV [%]	LHV [%]
PC350/5	2.9	2.8	0.6	1.1	2.9	2.9	2.9
PC450/5	5.3	5.0	1.2	1.1	2.9	6.7	6.4
PC550/5	7.7	7.3	1.9	1.1	2.9	10.4	9.9
PC650/5	13.6	12.4	2.9	1.1	2.9	16.6	15.3
PC350/100	3.7	3.5	0.5	1.1	2.9	2.6	2.5
PC450/100	8.6	8.1	1.6	1.1	2.9	8.9	8.4
PC550/100	11.1	10.3	2.2	1.1	2.9	12.2	11.4
PC650/100	12.9	11.9	2.7	1.1	2.9	15.1	14.0
WS350/5	5.1	5.0	1.1	1.0	2.5	6.5	6.4
WS450/5	6.0	5.8	1.6	1.0	2.5	9.9	9.5
WS550/5	8.3	7.8	2.6	1.0	2.5	16.0	15.2
WS650/5	12.4	11.5	4.5	1.0	2.5	28.2	26.3
WS350/100	3.8	3.6	0.6	1.0	2.5	4.0	3.9
WS450/100	6.2	5.9	1.4	1.0	2.5	8.7	8.3
WS550/100	8.8	8.2	2.1	1.0	2.5	13.3	12.4
WS650/100	11.1	10.2	2.9	1.0	2.5	18.5	17.1
WSP350/5	3.6	3.5	0.7	1.1	2.7	4.2	4.1
WSP450/5	5.9	5.6	1.4	1.1	2.7	7.7	7.4
WSP550/5	7.9	7.4	1.7	1.1	2.7	9.9	9.4
WSP650/5	9.9	9.2	2.6	1.1	2.7	15.1	14.1
WSP350/5	N/A	N/A	N/A	N/A	N/A	N/A	N/A
WSP450/100	9.1	8.4	2.3	1.1	2.7	13.6	12.7
WSP550/100	9.4	8.8	2.5	1.1	2.7	14.7	13.8
WSP650/100	13.4	12.3	4.0	1.1	2.7	23.9	22.1
SP350/0	3.2	3.1	0.6	0.9	2.5	3.7	3.6
SP650/0	10.2	9.5	2.3	0.9	2.5	15.6	14.7
SP350/0.3	3.0	2.9	0.7	0.9	2.5	4.6	4.4
SP650/0.3	8.9	8.3	2.7	0.9	2.5	18.0	16.9
SP350/0.6	4.3	4.2	1.1	0.9	2.5	7.1	6.9
SP650/0.6	9.5	8.9	3.1	0.9	2.5	20.8	19.5
WP350/0	2.2	2.1	0.3	1.1	2.6	1.7	1.7
WP650/0	9.8	9.2	1.9	1.1	2.6	11.6	10.9
WP350/0.3	3.2	3.1	0.6	1.1	2.6	3.4	3.3
WP650/0.3	7.4	6.9	1.8	1.1	2.6	11.0	10.4
WP350/0.6	4.8	4.7	0.7	1.1	2.6	4.4	4.3
WP650/0.6	12.1	11.2	2.9	1.1	2.6	17.4	16.3

* Gas weight basis

† Feedstock weight basis

The gas composition data for all five feedstock was used to investigate the influence of HTT on gas composition, as shown in Figure 6-1 (PC, WS and WSP) and Figure 6-2 (SP and WP). The larger concentration of CO and CO_2 at low HTT is mainly due to the breaking of carboxyl, carbonyl and ether groups as a result of hemicellulose and cellulose decomposition (Yang *et al.*, 2006b; Becidan *et al.*, 2007; Duman *et al.*, 2011; Chen *et al.*, 2012). Therefore at 350^{o}C CO and CO_2 represented over 94 % of the total gas produced. Figure 6-1 and Figure 6-2 show that with increasing HTT the concentration of H_2, CH_4 and C_2H_6 increased considerably while the concentration of CO_2 decreased. The reduced volume of CO_2 at elevated temperatures is due to the increased production of other gas species at higher HTT as well as the decreased formation of CO_2 above 450^{o}C. The reactions which lead to the formation of CO_2 are more favourable at lower temperature pyrolysis as they are a result of cellulose and hemicellulose decomposition (Di Blasi *et al.*, 1999; Fu *et al.*, 2011).The concentration of CO was found to peak between 350^{o}C – 450^{o}C for WS and 450^{o}C – 550^{o}C for PC and WSP while a substantial increase was seen in CO ($P < 0.0001$) for SP and WP pyrolysis as HTT was increased from 350^{o}C to 650^{o}C . Above 550^{o}C the fall in CO concentration was mainly due to the release of higher concentrations of H_2 and CH_4 as a result of lignin decomposition and vapour cracking rather than the reduced release of CO. Although CO and CO_2 are mainly released due to cellulose and hemicellulose decomposition at low HTT the degradation of lignin and secondary decomposition of volatiles at elevated temperatures have also been proposed to result in the release of CO and CO_2 (Duman *et al.*, 2011; Fu *et al.*, 2011; Chen *et al.*, 2012). The evolution of H_2 during pyrolysis can be attributed to thermal cracking of heavy hydrocarbons and aromatic condensation, mainly resulting from the increased thermal breakdown of lignin at higher pyrolysis temperatures (Yang *et al.*, 2006b; Chen *et al.*, 2012).

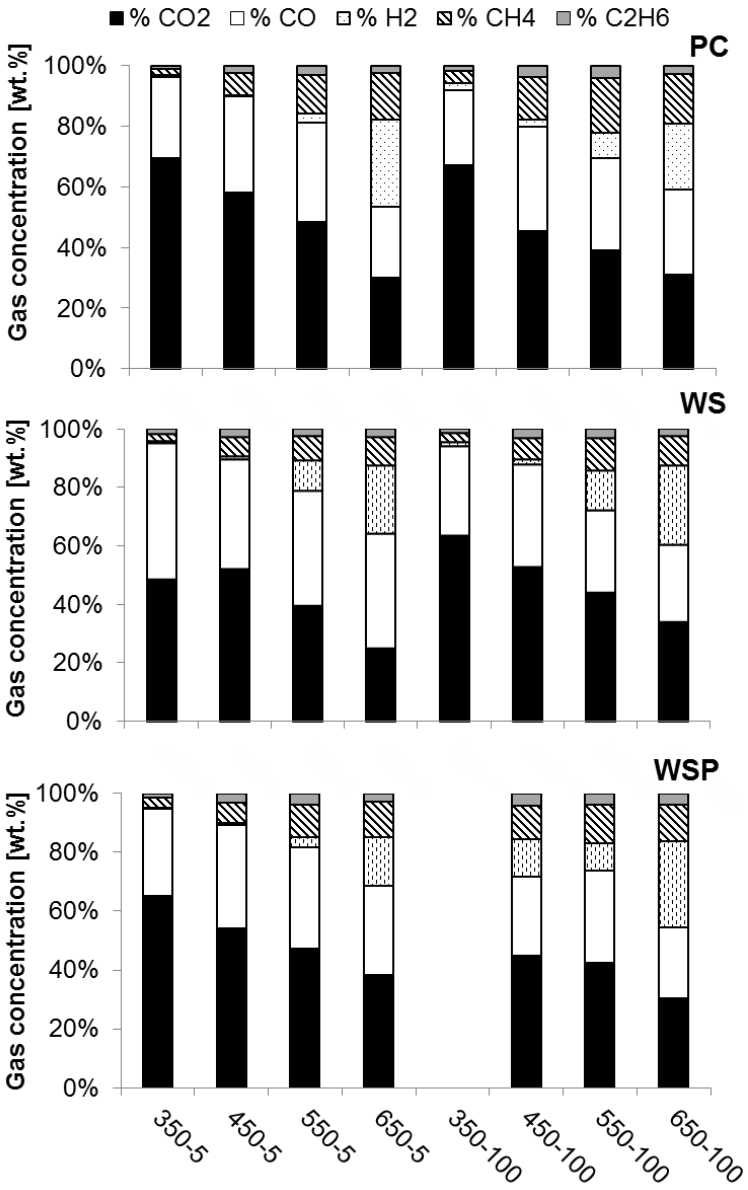

Figure 6-1: Influence of HTT and heating rate on the gas composition obtained from PC, WS and WSP pyrolysis. Composition corrected for dilution effect of carrier gas.

As shown in Figure 6-1 and Figure 6-2, at HTT $\leq$ 450^{o}C the concentrations of H_2 for all feedstock were relatively small (< 4 %); however as HTT was increased to 650^{o}C, the H_2 concentration increased substantially to maxima of 28.4 %, 27.1 %, 29.4 %, 17.3 % and 17.1 % for the pyrolysis of PC, WS, WSP, SP and WP respectively. Comparable values of H_2 concentration in pyrolysis gases have been reported in literature (Yang *et al.*, 2006b; Chen *et al.*, 2012). Similarly, with increasing HTT, the

concentration of CH_4 increased, as a result of secondary cracking of methoxyl (-O-CH_3) and methylene (-CH_2-) groups at elevated temperatures (Yang *et al.*, 2006b; Duman *et al.*, 2011; Fu *et al.*, 2011; Chen *et al.*, 2012). As the HTT was increased from 350°C to 650°C the concentration of CH_4 increased on average by 9.55 ± 3.4 vol. % (n = 11). The concentration of ethane was seen to only increase slightly (< 2.4 vol. %) as HTT was increased to 550°C, above which it then decreased due to the increased release of other gases. The increasing concentrations of H_2, CH_4 and C_2H_6 and decreasing CO_2 content as HTT was elevated from 350°C to 650°C resulted in significantly higher gas HHV ($P < 0.05$) as shown in Table 6-1.

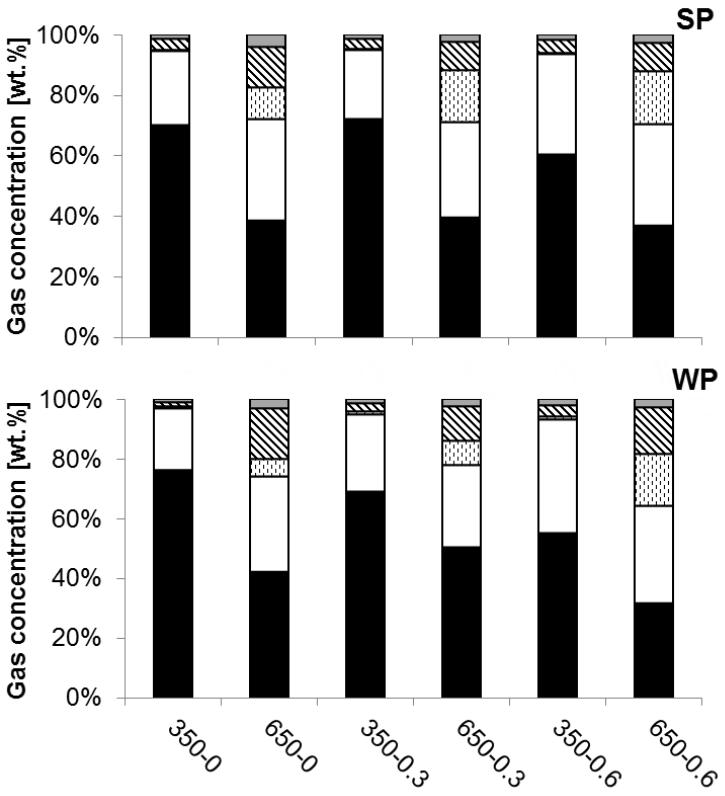

Figure 6-2: Investigating the effect of carrier gas flow rate and HTT on the gas composition of CO, H_2, CH_4, C_2H_6 and CO_2, measured from SP and WP experiments (Chapter 5). Composition corrected for dilution effect of carrier gas.

6.3.1.2 Heating rate

While the influence of temperature on gas composition has been extensively researched, as shown above, the same cannot be said for heating rate. There are a

limited number of investigations into the impact of heating rate on the composition of pyrolysis gas during slow pyrolysis (Williams & Besler, 1996; González *et al.*, 2003; Becidan *et al.*, 2007), since the majority of studies on heating rate are focused on the rapid heating involved in fast pyrolysis. This work covered a range of heating rates from $5^oC\ min^{-1}$ – $100^oC\ min^{-1}$. Only the gas composition data from PC, WS and WSP experiments, as shown in Figure 6-1, were used to investigate the influence of heating rate on gas composition.

Although temperature was seen as the most dominant variable in determining the release of gas species during pyrolysis, heating rate also influenced the concentrations of H_2 ($P = 0.041$), CO ($P = 0.012$), CH_4 ($P = 0.011$) and C_2H_6 ($P = 0.006$), while no statistically significant effect was seen for CO_2 ($P = 0.49$). Pyrolysis under a higher heating rate resulted in increased concentrations of H_2, CH_4 and C_2H_6. The concentration of H_2 peaked at 650^oC, while that of CH_4 and C_2H_6 peaked at 550^oC. On the other hand the higher heating rate reduced the CO concentration. As a result, the HHV of pyrolysis gas was higher ($P < 0.05$) for pyrolysis under higher heating rate. Low heating rates allow for the decomposition of biomass to progress through relatively distinct stages of moisture evolution and biomass decomposition (Yang *et al.*, 2006b). This slow evolution allows for gradual release of volatiles minimising the cracking of liquid products thus resulting in a peak emission of gas species followed by additional release over a longer period generating a double-maxima emission profile (Williams & Besler, 1996; González *et al.*, 2003; Becidan *et al.*, 2007). This double maxima is a result of the overlap in temperatures for the breakdown of hemicellulose and cellulose (González *et al.*, 2003). At higher heating rates ($\geq 80^oC\ min^{-1}$) the emission of the gas species differs greatly, with no double maxima observed but instead rapid decomposition of cellulose, hemicellulose and lignin occurring simultaneously (Williams & Besler, 1996; Becidan *et al.*, 2007). This advance decomposition of biomass components potentially lead to increased secondary reactions in the gas phase as well as secondary char decomposition, enhancing the formation of non-condensable gaseous products and increasing the overall gas yield (Demiral & Ayan, 2011).

6.3.1.3 Carrier gas flow rate

While the effect of carrier gas flow rate on product distribution has been reported in literature (Encinar *et al.*, 2000; Antal & Grønli, 2003; Demiral & Ayan, 2011; Demiral *et al.*, 2012; Crombie & Mašek, 2014), to the author's knowledge, no studies have been performed on how this production parameter can impact the composition of gas from slow pyrolysis. Only the gas composition data from SP and WP experiments, shown in Figure 6-2, was used to investigate the influence of carrier gas flow rate on gas composition. Increasing the carrier gas flow rate removes volatile matter faster from the hot zone, reducing secondary exothermic reactions such as thermal cracking, partial oxidation, depolymerisation and recondensation leading to decreased char formation (Encinar *et al.*, 2000; Demiral & Ayan, 2011; Demiral *et al.*, 2012). The results showed a clear statistically significant ($P < 0.01$) increase in H_2 and CO concentrations and gas HHV, as well as a decrease in CO_2 ($P < 0.0001$) with gas flow rate rising from 0 L min^{-1} to 0.66 $\pm$ 0.02 L min^{-1}. The effect of carrier gas flow rate was dependent on HTT. At low HTT (350^{o}C) the concentrations of CH_4 and C_2H_6 increased with increasing flow rate. However, at a higher temperature (650^{o}C) the concentration of H_2 increased when the carrier gas flow rate was raised from 0 L min^{-1} to 0.66 $\pm$ 0.02 L min^{-1}, while that of CH_4 and C_2H_6 decreased.

6.3.1.4 Feedstock

To compare the influence of all five biomass types on the gas composition, only the data obtained from pyrolysis at 350 and 650^{o}C, 5^{o}C min^{-1} and 0.33 $\pm$ 0.02 L min^{-1} were plotted in Figure 6-3. Feedstock was deemed to have no significant effect ($P > 0.05$) on any of the measured gas species. However the sets of experiments chosen for comparison of feedstock type only applied two HTTs, so the overall effect of feedstock could be masked due to the dominating influence of temperature at higher HTT. There is no clear trend between the pyrolysis gas composition and content of cellulose, hemicellulose and lignin found in the starting materials. However this is not surprising since all three biomass components can be responsible for increases in gas species. CO can be formed from the breakdown of hemicellulose at 300^{o}C,

cellulose at 450°C and lignin > 600°C, while CO_2 and CH_4 have also displayed multiple peaks in gas release associated with cellulose, hemicellulose and lignin (Yang *et al.*, 2007; Qu *et al.*, 2011). While lignin has been strongly associated with releasing the largest yields of H_2 and CH_4 (Yang *et al.*, 2007), when comparing the composition of all feedstocks, the highest concentrations of H_2 and CH_4 were released by PC which contained the lowest lignin content of 12.6 %. This indicates that the composition of gases released during pyrolysis is determined by a combination of the interactions between all biomass components rather than the concentration of any one component.

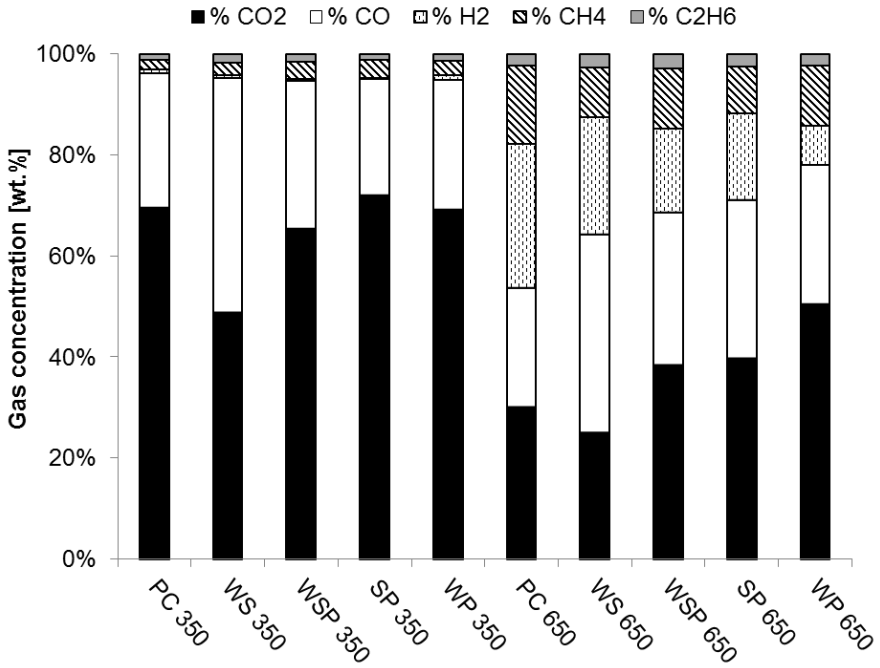

Figure 6-3: Evaluating the influence of feedstock selection on pyrolysis gas composition through the comparison of PC, WS, WSP, SP and WP pyrolysis at two HTTs, 5°C min^{-1} heating rate and 0.33 ± 0.02 L min^{-1} carrier gas flow rate.

To investigate the impact of mechanical pre-treatment of biomass (in this case pelleting), the difference in gas composition between WS and WSP pyrolysis was studied. Heat and mass transport mechanisms can play an important role in determining the amount and composition of the gases being released during pyrolysis (Di Blasi *et al.*, 1999; Becidan *et al.*, 2007). As particle size is reduced, the ease of

volatile matter release is increased, resulting in increased liquid and gas yields (Luo *et al.*, 2010). However, thicker biomass particles can lead to a temperature gradient within the particle resulting in a different core temperature compared to the surface temperature, resulting in increased char yields (Encinar *et al.*, 2000).

When the slower heating rate was applied, pyrolysis of WS material produced higher concentrations of H_2 and CO, while the pelleted material (WSP) produced higher concentrations of CH_4, C_2H_6 and CO_2. A combination of increased CO_2 content and reduced H_2 and CO present in the gas produced during WSP led to a higher gas heating value for the gas stream obtained during WS pyrolysis. However when applying the higher heating rate, the simultaneous decomposition of biomass components reduced the clarity of trends between pellet and non-pellet materials, with only CH_4 and C_2H_6 remaining the same as that seen for $5^oC\ min^{-1}$. No clear trend was visible for the concentrations of H_2 and CO, while CO_2 was higher in gas obtained from WS pyrolysis, resulting in a higher gas HHV for WSP pyrolysis when using $100^oC\ min^{-1}$. The density of the WS material was another important difference between the two biomass types since the lower density of WS resulted in a considerably smaller amount of feedstock being used for WS pyrolysis when compared to the same volume of WSP biomass. The physical properties of feedstock are therefore important when deciding the required reaction rate of pyrolysis, with smaller particles allowing a faster rate of heat transfer and therefore accelerating the pyrolysis process (Luo *et al.*, 2010) but minimising the duration of secondary reactions of volatiles.

6.3.2 **Self-sustaining system**

As the energy output/input of a pyrolysis process can change greatly with pyrolysis unit (type, scale etc.) and severity of pyrolysis (process temperature, heating rate etc.) it can be difficult to estimate reliably. Several studies have attempted to establish the theoretical energy required for the heat of pyrolysis (Daugaard & Brown, 2003; Bridgwater, 2006; Gronnow *et al.*, 2013; Yang *et al.*, 2013). Among these studies, the lowest estimated energy required to sustain the pyrolysis process was calculated by Gronnow et al. (2013) to be 6 % of biomass HHV or roughly 1.17

MJ kg^{-1}, while Bridgwater (2006) proposed a higher proportion of 15 %. Gronnow *et al.* (2013) estimated the energy input for pyrolysis of 1 ton of wood chips to be 1173 MJ. This was done by separating the pyrolysis process into three stages (heating, vaporisation and pyrolysis), as shown in Figure 6-4.

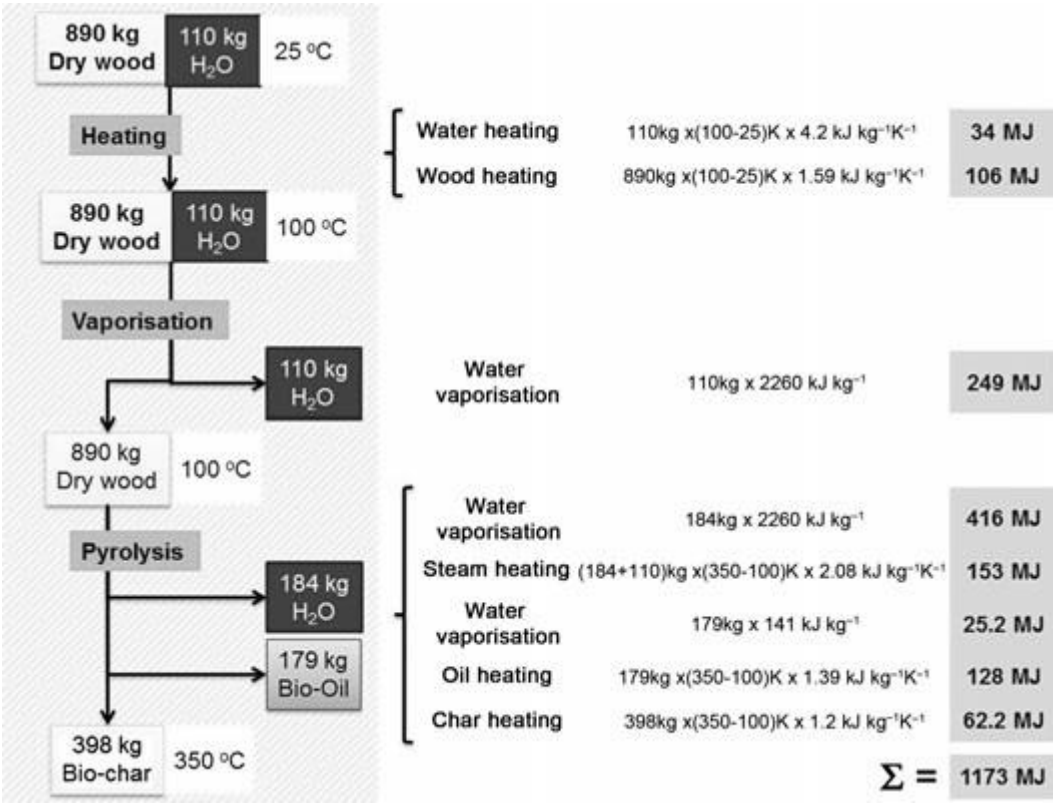

Figure 6-4: Estimation of energy efficiency of slow pyrolysis

As the lower energy limit (6% biomass HHV) taken from Gronnow *et al.* (2013) was calculated for pyrolysis at 350°C, pyrolysis at higher temperatures would be expected to require more input energy. For that reason the values calculated by Daugaard and Brown (2003) (1.3 – 1.5 MJ kg^{-1}) and Yang et al. (2013) (1.1 – 1.6 MJ kg^{-1}) were based on pyrolysis at 500°C and 550°C respectively and still fell within the 6 – 15 % range. Therefore, in this work we used the range of 6 – 15 % of biomass HHV as the theoretical energy required to sustain the heat of pyrolysis. To assess under which conditions the energy contained in the pyrolysis gas would be sufficient to sustain the pyrolysis process, we compared the energy content of the pyrolysis gas, under different processing conditions, with the lower (6 % biomass HHV) and the upper

estimates (15 % biomass HHV). The energy content of gas was calculated from the gas LHV rather than HHV, since LHV demonstrates the energy which can be extracted by combustion of the gas/fuel in a system that cannot utilise the condensation heat of water, i.e. standard combustion and engines. The energy content of gas was compared and the upper/lower limits found in literature were compared in Table 6-1.

The lower limit of 6 % was consistently satisfied by the energy contained in all pyrolysis gases produced at HTT $\geq$ 450^{o}C, indicating that pyrolysis under these conditions would yield pyrolysis gas with enough energy to heat the pyrolysis reactor. However, pyrolysis under most conditions investigated in this study would fail to meet the higher energy limit (15 % biomass HHV). The only conditions under which the upper limit was achieved were when applying a HTT of 650^{o}C for both heating rates when using WS biomass, while PC and WSP only surpassed 15 % when the higher heating rate was applied. Although the gas stream produced during pyrolysis at 550^{o}C failed to reach the required energy output of the upper energy limit it did surpass the required limits reported by Daugaard and Brown (2003) and Yang et al. (2013). Of the selected energy limits, the upper limit of 15 % was obtained from a 'fast pyrolysis' study and provided no evidence for its value; thus any pyrolysis conditions which surpasses the other remaining energy limits were still deemed to be important to achieving a self-sustaining system.

In the cases where the energy content of the pyrolysis gas surpassed that needed to sustain the pyrolysis process, additional energy could be available to drive other steps in the pyrolysis process. The most important step is the pre-drying of biomass material prior to pyrolysis. In addition to the energy content of the gas stream, the CGE of the system was also calculated to demonstrate the efficiency of the transfer of energy stored within the feedstock to that in the final gas stream. The CGE is commonly used for comparison of different gasification and pyrolysis systems. Both the CGE based on gas HHV and gas LHV increased as HTT rose from 350^{o}C – 650^{o}C, with the larger difference between HHV CGE and LHV CGE also increasing with temperature. Pyrolysis of WS at 650^{o}C using the lower heating rate resulted in

gas with the largest energy content, and therefore also generated the highest CGE for both HHV (28.2 %) and LHV (26.3 %). Although the CGE range is substantially lower than values obtained for gasification (30 – 70 % (Cao *et al.*, 2006)) this is not unexpected since during slow pyrolysis the majority of the biomass energy content is recovered within the char and liquid products rather than the gas product. While the results presented within this chapter set important considerations for the future selection of pyrolysis conditions, the yields and energy values calculated within this work were achieved using a small-scale batch pyrolysis unit. Therefore further studies involving large scale pyrolysis and detailed LCA are needed before all the implications of these results can be fully understood.

6.4 Conclusion

For identifying the most suitable set of production conditions the product yields, properties of liquid and biochar products as well as end market for co-products all need to be considered in detail, as large differences in product properties can occur between 450 and 650^{o}C, as seen in Chapters 3, 4 and 5. However, for the range of conditions investigated, pyrolysis at HTTs $\geq$ 450^{o}C consistently, for all production conditions, produced a gas product with sufficient energy content to meet the lower energy limit for maintaining the pyrolysis process, while the upper energy limit was only reached for pyrolysis at 650^{o}C. Whether a pyrolysis system is optimised for the production of biochar and/or bio-oils, sustaining the pyrolysis process solely by combustion of the gas stream would increase the potential to utilise biochar and pyrolysis liquids for high-value products, and also reduce the carbon footprint of the pyrolysis system and associated products.

Chapter 7. **Predicting the properties of biochar**

Chapter 7 is not currently intended for publication and so does not follow the normal format of a paper chapter. However the candidate was still responsible for all data analysis and writing the chapter. Support and guidance in the data analysis was provided by statistician Giles Innocent while contributions to the editing of the chapter were also made by Giles Innocent as well as Ondřej Mašek.

7.1 Introduction

Feedstock is arguably one of the most important variables when determining the final composition and properties of biochar, bio-oil and pyrolysis gas since these are derived from the breakdown of cellulose, hemicellulose and lignin during pyrolysis. A vast number of different types of biomass have been used for biochar production, however the identification of relationships between the feedstock components (cellulose, hemicellulose, lignin and ash), process conditions (HTT, heating rate etc.) and important biochar properties such as C stability and labile-C content is still absent from literature. Therefore the cellulose, hemicellulose and lignin content of several biomass types (PC, RH, SP, WP, WS, WSP) used throughout this thesis were determined and used for statistical analysis to investigate any relationships between the biomass composition and key biochar properties of stable-C concentration and stable-C yield. By identifying any relationships between the initial feedstock characteristics and final biochar properties, the engineering of biochar production for enhancing selected properties can be expanded to include the starting material. Understanding how the components of biomass can influence important functional properties, such as biochar stability, would mean any screening process to determine the effectiveness of a specific biochar could then be initially assessed on the composition of biomass rather than the final biochar product. This would save extensive time and resources spent producing biochar which might have a limited effect or unfavourable characteristics.

Through four separate "fully crossed design" experiments presented in Chapters 3, 4, 5 and 6, the influence that pyrolysis conditions have on biochar properties was investigated. Throughout these studies feedstock was identified as a statistically significant parameter for determining several of biochar's properties. Therefore the aim of this chapter is to combine the results of the previous chapters into one data set and uses this data set to develop statistical models to enable the prediction of biochar properties through linear regression, thus addressing Objective 4 in section 1.7.

7.2 Results and discussion

7.2.1 Predicting the stable-C concentration of biochar

7.2.1.1 Determining the best model

The best model for predicting the stable-C concentration of biochar was selected by running the 'Best Subsets' procedure within Minitab. The generated results, displayed in Figure 7-1, showed the outcome of each potential combination of variables to determine the best fit.

Vars	R-Sq	R-Sq(adj)	Mallows Cp	S	Temperature	Heating rate	Feedstock	Feedstock	Carbonisation	Holding time	Reactor	Feedstock	Activation	Feedstock
1	79.7	79.3	45.0	9.6312	X									
1	1.6	0.1	459.3	21.181										X
2	80.9	80.3	40.7	9.4169	X									X
2	80.4	79.8	43.0	9.5230	X	X								
3	82.9	82.0	32.0	8.9783	X								X	X
3	82.4	81.6	34.4	9.0990	X			X		X				
4	86.7	85.9	13.5	7.9666	X				X	X	X			
4	84.0	83.0	27.9	8.7428	X	X							X	X
5	88.9	88.0	3.8	7.3367	X				X	X	X		X	X
5	88.5	87.5	6.2	7.4848	X			X	X	X	X			
6	89.1	88.0	5.1	7.3528	X		X			X	X		X	X
6	89.0	87.9	5.3	7.3669	X			X		X	X		X	X
7	89.1	87.9	6.6	7.3837	X		X	X		X	X		X	X
7	89.1	87.8	6.7	7.3900	X	X	X			X	X		X	X
8	89.2	87.7	8.2	7.4219	X	X	X	X		X	X		X	X
8	89.2	87.7	8.3	7.4294	X		X	X	X	X	X		X	X
9	89.3	87.6	10.0	7.4720	X	X	X	X	X	X	X		X	X

Figure 7-1: Best subset procedure results for determining the most suitable model for predicting stable-C%. Screen shot of statistical analysis taken from Minitab 16.

When evaluating the suitability of the fit, the highest r^2 adjusted value is important. However, as adding more variables to the model will always add complexity to the model, the final selection should be based on the model with the highest r^2 adjusted value and the lowest Mallow's C-p value. The Mallow's C-p value represents the

amount of error left unexplained by a model, so 'less is more' in this case. Based on this combined selection process, the best suited model for predicting stable-C included five variables: HTT, cellulose, hemicellulose, lignin and feedstock ash content. By removing the variable of ash content the model can be simplified, but this also results in a slightly lower r^2 adjusted value and higher Mallow's C-p. As decreasing the complexity of the model should improve the ease of application, both models were used to generate a regression equation for predicting stable-C concentration, with the most suitable model being decided by the highest modelling efficiency (EF) (Loague & Green, 1991). The EF is a method of evaluating how well a set of predicted values, determined by a model, fit to observed values. This efficiency is determined by the following equation:

$$EF = \frac{(\sum^{n}(O - \bar{O})^2 - \sum^{n}(P - O)^2)}{\sum^{n}(O - \bar{O})^2}$$

Where *n* is the number of samples; *O* are the observed values; $\bar{O}$ is the mean of the observed data; and *P* is the predicted values.

7.2.1.2 **Linear regression**

Looking for relationships and attempting to explain the variation in observations are two of the staples of data analysis. Linear regression tries to find relationships between two or more variables to build a model which attempts to describe that relationship. The most basic of regression models is the simple linear regression model. Therefore when entering the two models identified in section 7.2.1.1, two regression equations (M1 and M2) for predicting stable-C content were generated using 67 data observations, as seen in Figure 7-2 and Figure 7-3.

```
The regression equation is
Stable C % = - 368 + 0.140 Temperature + 4.41 Cellulose + 4.06 Hemicellulose
             + 3.79 lignin - 0.781 Feedstock Ash


Predictor          Coef   SE Coef      T      P
Constant        -367.98     64.37  -5.72  0.000
Temperature    0.140387  0.006738  20.83  0.000
Cellulose        4.4082    0.7776   5.67  0.000
Hemicellulose    4.0625    0.7075   5.74  0.000
lignin           3.7917    0.6031   6.29  0.000
Feedstock Ash   -0.7808    0.2245  -3.48  0.001


S = 7.33672   R-Sq = 88.9%   R-Sq(adj) = 88.0%


Analysis of Variance

Source          DF       SS      MS      F      P
Regression       5  26354.3  5270.9  97.92  0.000
Residual Error  61   3283.5    53.8
Total           66  29637.7
```

Figure 7-2: Linear regression model for predicting stable-C% containing the variables of temperature, cellulose, hemicellulose, lignin and feedstock ash content. Screen shot of statistical analysis taken from Minitab 16.

```
The regression equation is
Stable C % = - 385 + 0.141 Temperature + 4.69 Cellulose + 4.34 Hemicellulose
             + 3.45 lignin


Predictor          Coef   SE Coef      T      P
Constant        -384.90     69.70  -5.52  0.000
Temperature    0.141220  0.007312  19.31  0.000
Cellulose        4.6933    0.8396   5.59  0.000
Hemicellulose    4.3363    0.7634   5.68  0.000
lignin           3.4525    0.6463   5.34  0.000


S = 7.96658   R-Sq = 86.7%   R-Sq(adj) = 85.9%


Analysis of Variance

Source          DF       SS      MS       F      P
Regression       4  25702.8  6425.7  101.25  0.000
Residual Error  62   3934.9    63.5
Total           66  29637.7
```

Figure 7-3: Linear regression model for predicting stable-C% containing the variables of temperature, cellulose, hemicellulose and lignin. Screen shot of statistical analysis taken from Minitab 16.

The number in front of each variable in the regression equation indicates the coefficient of the variable and represents the change in the output (stable-C %)

associated with a one-unit increase in each variable (e.g. stable-C % increased 0.14 % for every increase of 1^{o}C). One effective way of evaluating the performance and fit of the model is the difference between observed and predicted values (Loague & Green, 1991). This approach can include using the coefficient of determination, or r^2. Both models show a high level of fit based on r^2 adjusted values of > 85 %. However r^2 is not always regarded as the most accurate assessment therefore the EF was also calculated based on the equation proposed by Loague & Green (1991). The EF for each model was calculated and compared in Table 7-1.

Table 7-1: Comparison of modelling efficiency between best fit models for predicting stable-C concentration.

Model	Components	EF
M1	HTT, cellulose, hemicellulose, lignin and feedstock ash	0.889
M2	HTT, cellulose, hemicellulose and lignin	0.867

Table 7-1 shows that for this data set the more complex model containing five variables produced a better fit of predicted to observed values for stable-C concentration. This is not surprising as an additional variable can help to account for more of the variation in the predicted values. However the difference between the models is minute.

As discussed earlier in the thesis, biomass pyrolysis proceeds through a series of complex reactions depending on the relative proportions of biomass components (cellulose, hemicellulose and lignin) within the feedstock. The proportion of these components has also been attributed to changes in co-product distribution and properties. The pyrolysis of hemicellulose and cellulose occurs rather rapidly compared to lignin (160^{o}C – 900^{o}C), with the majority of hemicellulose weight loss occurring below 315^{o}C and cellulose between 315^{o}C – 400^{o}C (Yang *et al.*, 2007). The thermal degradation of lignocellulosic materials is poorly modelled by simple kinetic laws although the most promising results seem to be obtained from kinetic models consisting of independent simultaneous reactions (Orfao *et al.*, 1999). Many authors consider that general biomass pyrolysis follows a superposition of the

independent kinetics of the primary biomass components of cellulose, hemicellulose and lignin (Miller & Bellan, 1997; Orfao *et al.*, 1999; Manyà *et al.*, 2003; Yang *et al.*, 2007). Manya *et al.* (2003) expand this claim further and state that the global production of volatile matter also corresponds to the summation of the individual contributions from the three natural polymers. As cellulose is typically the major component of dry biomass fuels (50 % by weight) and the most abundant organic compound in the world, the kinetics of cellulose pyrolysis are of high interest and therefore is most frequently investigated (Antal & Varhegyi, 1995; Di Blasi, 1998; Orfao *et al.*, 1999).

The decomposition of cellulose can be separated into three main chemical pathways determined by temperature variation. At low temperatures the first pathway is the formation of anhydrocellulose through a reduction in the degree of polymerization. As temperature is increased the depolymerisation stage is followed by two competing degradation reactions resulting in char and gas formation at < 573 K (ring scission) or vapour-phase tar formation at > 573 K (end-group depolymerisation) (Di Blasi, 1998). A further study into biomass decomposition by Orfao *et al.* (1999) showed cellulose decomposition was first measured at 225^{o}C with the majority of transformation occurring within a narrow temperature range. The final residue produced was only 5 % of the initial mass used, demonstrating a high volatile matter content of cellulose. This observation is also made by Qu *et al.* (2011) who studied the outcome of gas, liquid and char properties from the pyrolysis of cellulose, xylan (hemicellulose) and lignin separately as well as three biomass samples. Analysis of the biomass components showed the order of fixed C and volatile matter concentrations to be lignin > xylan > cellulose and cellulose > xylan > lignin respectively, which contributed to cellulose also demonstrating the largest yield of bio-oil and lowest char yield. Bio-oil produced from cellulose was also more susceptible to decomposition at higher temperatures, resulting in increased secondary cracking of oil during cellulose pyrolysis compared to lignin and xylan. The secondary cracking of bio-oil resulted in increased gas release, with lignin pyrolysis producing the lowest gas yield and hemicellulose reaching the highest value below

560^{o}C; while cellulose demonstrated a higher yield above 560^{o}C. Qu *et al.* (2011) also described the different evolution of gas species from each biomass component, providing additional variation of interactions with the gas stream influencing the final products from pyrolysis.

A study into the decomposition of xylan (hemicellulose) by Di Blasi & Lanzetta (1997) demonstrated that the process occurs in two stages. Firstly hemicellulose degrades at low temperature very rapidly to produce high volatile release and char formation. The second stage occurs at above 270^{o}C and involves further degradation of the solid product, resulting in increased char formation and volatile formation. Orfao *et al.* (1999) found xylan (hemicellulose) decomposition began at a lower temperature (160^{o}C) than that of cellulose; however the decomposition curves were similar to those of cellulose. Xylan also demonstrated a lower volatile yield compared to cellulose, resulting in the conclusion that hemicellulose made a relatively important contribution to the formation of char during biomass pyrolysis. Finally the decomposition of lignin actually started at the lowest temperature (110^{o}C), but the overall decomposition occurred over an extensive temperature range (up to 900^{o}C) at a low rate; thus lignin was attributed to the main contribution of final char yield. Therefore the inclusion of cellulose, hemicellulose and lignin in the statistical prediction of stable-C is not surprising since these components are the determining factors in the chemical reactions occurring during pyrolysis and the final yields and properties of pyrolysis co-products.

The presence of feedstock ash should also be given more consideration in determining the final outcome of the model. The presence of inorganic matter in the biomass structure has led to rough approximations of the pyrolysis kinetics since ash content can act as a catalyst or an inhibitor for the degradation of biomass components (Di Blasi, 1998). The use of individual biomass components or even synthetic biomass for pyrolysis is different to that of natural biomass, due to the presence of this mineral matter in natural biomass. Several studies have shown the significant effect that the mineral content of biomass can have on the chemical reactions occurring during pyrolysis, in particular the devolatilisation rate and initial

decomposition temperature of biomass components (Antal & Varhegyi, 1995; Raveendran *et al.*, 1995; Williams & Horne, 1995; Yang *et al.*, 2006a; Qu *et al.*, 2011). Raveendran *et al.* (1995) found that the removal of mineral matter resulted in an increase in devolatilisation rate, while also raising the initial decomposition temperature for all cases. The higher concentration of ash present within biomass also lowered the bio-oil yield and increased the yield of char (Qu *et al.*, 2011). This was further demonstrated in natural biomass, when rice husk containing low lignin content actually produced the highest char yield due to its significantly higher ash concentration (Qu *et al.*, 2011). Therefore the biomass components are not independent of each other and each one can be affected by ash content, making the task of predicting the outcome of pyrolysis from biomass composition a difficult and complicated procedure, especially when biomass composition can vary greatly between species as well as within the same species as habitat, age and fraction (trunk, branches, roots etc.) change (Raveendran, 1996; Orfao *et al.*, 1999; Qu *et al.*, 2011).

From the data set collected during this PhD, cellulose, hemicellulose and lignin can be used in conjunction with pyrolysis HTT and feedstock ash concentration as part of a model to generate a strong prediction of biochar stable-C concentration. However as described in Vassilev *et al.* (2010) there are many more components which make up biomass than just cellulose, hemicellulose, lignin and ash. These include metals (Ca, K, Mg etc.), inorganic minerals (phosphates, silicates, chlorides, nitrates etc.) and fluid matter such as moisture, gas and gas liquid inclusions, which could all affect the reactions occurring during pyrolysis, not to mention the variation in the kinetics of pyrolysis with production conditions.

7.2.2 **Predicting the stable-C yield of biochar**

As discussed in Chapters 3, 4 and 5 it is in fact the yield of stable-C rather than the stable-C concentration of biochar which is more important for assessing the C sequestration potential of biochar. For that reason the 'Best Subsets' procedure and linear regression modelling were repeated (still using 67 observations) to assess the fit of a model for predicting the stable-C yield of biochar based on pyrolysis conditions and feedstock composition. The outcome of the 'Best Subsets' analysis, seen in Figure 7-4, identified the best fit of variables for predicting stable-C yield to be HTT, heating rate, flow rate and the feedstock ash content (Figure 7-5).

					Temperature	Heating rate	Feedstock	Flow rate	Cellulose	Hemicellose	Feedstock Ash
Vars	R-Sq	R-Sq(adj)	Mallows Cp	S							
1	37.5	36.5	34.0	9.0565	X						
1	20.4	19.2	60.4	10.217							X
2	59.0	57.7	2.6	7.3885	X						X
2	50.3	48.7	16.2	8.1407	X					X	
3	60.7	58.9	1.9	7.2904	X		X				X
3	60.2	58.3	2.8	7.3426	X	X					X
4	61.9	59.4	2.2	7.2416	X	X		X			X
4	61.0	58.5	3.5	7.3243	X		X			X	X
5	62.3	59.2	3.5	7.2619	X	X		X		X	X
5	62.2	59.1	3.6	7.2657	X	X		X	X		X
6	62.9	59.2	4.5	7.2595	X			X	X	X	X
6	62.6	58.8	5.0	7.2920	X	X		X	X		X
7	63.1	58.8	6.2	7.2992	X	X		X		X	X
7	63.0	58.6	6.4	7.3102	X			X	X	X	X
8	63.2	58.1	8.1	7.3535	X	X		X	X	X	X
8	63.2	58.1	8.1	7.3581	X	X	X	X		X	X
9	63.3	57.5	10.0	7.4138	X	X	X	X	X	X	X

Figure 7-4: Best subset procedure results for determining the most suitable model for predicting stable-C yield. Screen shot of statistical analysis taken from Minitab 16.

```
The regression equation is
Stable C Yield (Feed C%) = 11.9 + 0.0530 Temperature - 0.0306 Heating rate
                           - 7.46 Flow rate + 0.888 Feedstock Ash


Predictor          Coef   SE Coef      T      P
Constant         11.852     3.940   3.01  0.004
Temperature    0.052962  0.006651   7.96  0.000
Heating rate  -0.03056   0.02245  -1.36  0.178
Flow rate       -7.455     4.479  -1.66  0.101
Feedstock Ash   0.8879    0.1475   6.02  0.000


S = 7.24155   R-Sq = 61.9%   R-Sq(adj) = 59.4%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       4  5275.8  1318.9  25.15  0.000
Residual Error  62  3251.3    52.4
Total           66  8527.1
```

Figure 7-5: Linear regression model for predicting stable-C yield containing the variables of temperature, heating rate, flow rate, hemicellulose and feedstock ash content. Screen shot of statistical analysis taken from Minitab 16.

Unlike M1 and M2, the best fit regression model for predicting stable-C yield (M3) was shown to not include cellulose, hemicellulose and lignin. Alternative models were possible which include the variables of cellulose (M4) and hemicellulose (M5), however this would add complexity to the model. The model which contained cellulose produced higher EF, as seen in Table 7-2; however the difference is minimal and expected when additional variables are added to the model.

Table 7-2: Comparison of modelling efficiency between best fit models for predicting stable-C yield

Model	Components	EF
M3	HTT, heating rate, carrier gas flow rate and feedstock ash	0.619
M4	HTT, heating rate, carrier gas flow rate, cellulose and feedstock ash	0.622
M5	HTT, heating rate, carrier gas flow rate, hemicellulose and feedstock ash	0.536

Therefore M3 would be the preferred model due to the relative ease of measuring the ash concentration of feedstock compared to the cellulose or hemicellulose content. The EF of models M3, M4 and M5 only provided a moderate fit to the observed results for stable-C yield. The fit of a model could be affected by outlying values caused by unexpected or unusual observations. However by gathering a larger data set based on additional feedstock and production conditions, such unusual observations can become clearer which will aid in improving the strength of the models.

7.2.3 Regression models for predicting the HHV of pyrolysis co-products

Although biochar stability was studied throughout this thesis, the heating value of biochar was only investigated within Chapter 5 and so only the data for those biochar samples was included in the determination of biochar HHV (36 observations). The determination of gas HHV was covered in Chapter 5 and Chapter 6 and so included a larger number of samples for consideration (59 observations). As liquid samples were not analysed for composition there were no available data to predict the liquid HHV and thus liquids are not discussed in the following section.

7.2.3.1 Biochar HHV

While the HHV of biomass can be measured through bomb calorimetry, this involves specialised and expensive equipment. Therefore the heating value of biomass is commonly estimated by using calculations based on the chemical properties of biomass. Several researchers have therefore used the results of ultimate analysis (C, H, N and O content) and proximate analysis (fixed C, volatile matter and ash content) to formulate regression equations for estimating the HHV of lignocellulosic materials, as shown in Table 7-3.

Table 7-3: Several regression equations obtained from literature which use the results of ultimate analysis (C, H, N and O) and proximate analysis (fixed C (FC), volatile matter (VM) and ash content) to estimating HHV of biomass.

Equation	Regression Equation (HHV, MJ/kg)	Reference
E1	HHV = ((0.335 × C) + (1.423 × H) - (1.54 × O) - (1.45 × N))	(Demirbas, 1997)
E2	HHV = (0.2949 × C) + (0.8250 × H)	(Yin, 2011)
E3	HHV = -1.3675 + (0.3137 × C) + (0.7009 × H) + (0.0318 × O)	(Sheng & Azevedo, 2005)
E4	HHV = (0.196 × FC) + 14.119	(Demirbas, 1997)
E5	HHV = 35.43 - (0.1835 × VM) - (0.3543 × Ash)	(Cordero *et al.*, 2001)
E6	HHV = (0.3536 × FC) + (0.1559 × VM) - (0.0078 × Ash)	(Parikh *et al.*, 2005)
E7	HHV = (0.1905 × VM) + (0.2521 × FC)	(Yin, 2011)
E8	HHV = 19.288 - (0.2135 VM/FC) - (1.9584 Ash/VM) + (0.0234 FC/Ash)	(Nhuchhen & Abdul Salam, 2012)

In Chapter 5 the HHV of the systematic set of biochar samples was measured using bomb calorimetry (Table 5-2). Therefore in the following section these measured values of HHV were compared to the values calculated by using E1 – E8 as well as new models developed below. The new models were determined through linear regression based on the process conditions (HTT, residence time and carrier gas flow rate) as well as the ultimate and proximate analysis results. However, since the results of ultimate analysis and proximate analysis are highly correlated, the regression model only allowed the inclusion of one type of analysis results at a time. Therefore each set of analytical data was addressed separately to see which generated the model of best fit.

7.2.3.2 Ultimate analysis

As previously discussed, the first step in producing a linear regression model is determining the 'Best Subsets' from which the regression model will be generated. The generated results, displayed in Figure 7-6, showed the outcome of each potential combination of variables to determine the best fit model for predicting biochar HHV based on production conditions and the concentration of C, H, N and O.

Vars	R-Sq	R-Sq(adj)	Mallows Cp	S	Temperature	Residence time	Flow rate	% C	% H	% N	% O
1	81.9	81.4	65.7	1.7606				X			
1	68.0	67.1	140.6	2.3396						X	
2	94.3	94.0	0.6	1.0007				X			X
2	92.9	92.5	8.4	1.1202				X		X	
3	94.5	94.0	1.5	0.99671				X		X	X
3	94.5	94.0	1.5	0.99755		X	X				X
4	94.7	94.0	2.5	0.99561		X	X			X	X
4	94.6	93.9	3.0	1.0043	X		X			X	X
5	94.8	93.9	4.0	1.0034	X	X	X			X	X
5	94.7	93.8	4.5	1.0119		X	X	X	X	X	
6	94.8	93.7	6.0	1.0204	X	X	X	X	X	X	
6	94.8	93.7	6.0	1.0206	X	X	X	X		X	X
7	94.8	93.5	8.0	1.0385	X	X	X	X	X	X	X

Figure 7-6: Best subset procedure results for determining the most suitable model for predicting Biochar HHV using production conditions and ultimate analysis results. Screen shot of statistical analysis taken from Minitab 16.

Based on the selection criteria of largest r^2 adjusted value and the lowest Mallow's C-p, the best fit model only included biochar C and O concentration. Therefore when entering these variables the regression model (M6), as seen in Figure 7-7, was generated.

```
The regression equation is
Char CV (MJ/Kg) = - 7.55 + 0.439 %C + 0.211 %O


Predictor      Coef  SE Coef      T      P
Constant     -7.552    1.646  -4.59  0.000
%C          0.43885  0.01944  22.58  0.000
%O          0.21069  0.02479   8.50  0.000


S = 1.00069   R-Sq = 94.3%   R-Sq(adj) = 94.0%


Analysis of Variance

Source           DF      SS      MS       F      P
Regression        2  548.95  274.48  274.10  0.000
Residual Error   33   33.05    1.00
Total            35  582.00
```

Figure 7-7: Linear regression model for predicting Biochar HHV containing the variables of biochar C and O concentration. Screen shot of statistical analysis taken from Minitab 16.

The r^2 adjusted value of 94% demonstrated a very strong fit of the predicted values against the observed HHV. However, as previously discussed, the determination of EF may be a more accurate demonstration of the model's fit. As seen in Table 7-4, the EF was calculated to be 0.94 confirming the strong fit of the model with the observed values of biochar HHV.

Table 7-4: Model efficiency of linear regression model for predicting biochar HHV based on ultimate analysis results.

Model	Components	EF
M6	C% and O%	0.943

This regression model could therefore provide a quick and cheap alternative to determining the HHV of biochar, through applying the data obtained from the common analytical technique of CHNO analysis without needing the relatively expensive bomb calorimetry analysis needed to determine heating value.

7.2.3.3 **Proximate analysis**

Using biochar C and O content produced a strong model to predict biochar HHV however the results of proximate analysis have also been proposed as an alternative for predicting the heating value of biochar (Demirbas, 1997; Cordero *et al.*, 2001; Parikh *et al.*, 2005; Yin, 2011; Nhuchhen & Abdul Salam, 2012). Therefore the same steps were carried out for proximate analysis results to compare the strength of the two linear regression models. The 'Best Subsets' analysis displayed in Figure 7-8 was compiled from production condition variables and proximate analysis results.

Vars	R-Sq	R-Sq(adj)	Mallows Cp	S	Temperature	Residence time	Flow rate	Ash	Fixed C
1	59.5	58.3	233.0	2.6339				X	
1	50.6	49.1	291.2	2.9089					X
2	95.1	94.8	1.9	0.92730				X	X
2	90.7	90.1	31.1	1.2841	X			X	
3	95.3	94.9	2.7	0.92443	X			X	X
3	95.2	94.8	3.2	0.93183		X	X	X	X
4	95.4	94.8	4.3	0.93247	X		X	X	X
4	95.4	94.8	4.4	0.93421	X	X		X	X
5	95.4	94.6	6.0	0.94344	X	X	X	X	X

Figure 7-8: Best subset procedure results for determining the most suitable model for predicting biochar HHV using production conditions and proximate analysis results. Screen shot of statistical analysis taken from Minitab 16.

Due to the high correlation between fixed C and volatile matter only one of these variables can be included within the model, however the results of the model are the same for both variables. From Figure 7-8 the best fit model was produced using only biochar ash content and fixed C concentration, while temperature, ash content and fixed C concentration also showed a high r^2 adjusted value as well as flow rate, fixed

C and ash content. However both the variables of temperature and carrier gas flow rate are not deemed to be significant in their respective models due to $P > 0.05$, as seen in Figure 7-9 for temperature.

The regression equation is
Char CV (MJ/Kg) = 19.2 - 0.00390 Temperature - 0.286 Ash + 0.187 Fixed C

Predictor	Coef	SE Coef	T	P
Constant	19.1502	0.9634	19.88	0.000
Temperature	-0.003895	0.003548	-1.10	0.280
Ash	-0.28598	0.02615	-10.94	0.000
Fixed C	0.18711	0.03325	5.63	0.000

S = 0.924429 R-Sq = 95.3% R-Sq(adj) = 94.9%

Analysis of Variance

Source	DF	SS	MS	F	P
Regression	3	554.65	184.88	216.35	0.000
Residual Error	32	27.35	0.85		
Total	35	582.00			

Figure 7-9: Linear regression model for predicting biochar HHV containing the variables of temperature, biochar ash content and fixed C concentration. Screen shot of statistical analysis taken from Minitab 16.

Therefore the best fit model, M7, only contained fixed C concentration and ash content as seen in Figure 7-10.

```
The regression equation is
Char CV (MJ/Kg) = 19.8 + 0.152 Fixed C - 0.307 Ash


Predictor      Coef   SE Coef       T      P
Constant    19.8266    0.7429   26.69  0.000
Fixed C    0.152217  0.009799   15.53  0.000
Ash        -0.30719   0.01769  -17.37  0.000


S = 0.927300   R-Sq = 95.1%   R-Sq(adj) = 94.8%


Analysis of Variance

Source          DF      SS      MS       F      P
Regression       2  553.62  276.81  321.92  0.000
Residual Error  33   28.38    0.86
Total           35  582.00
```

Figure 7-10: Linear regression model for predicting biochar HHV containing the variables of fixed C concentration and biochar ash content. Screen shot of statistical analysis taken from Minitab 16.

The EF of M7 (Table 7-5) demonstrated a slightly higher degree of fit for predicting biochar HHV compared to M6, indicating the potential strength of using proximate analysis data over ultimate analysis. Proximate analysis is also performed using simpler laboratory equipment which may also influence the final selection of the desirable model.

Table 7-5: Comparison of the model efficiencies for predicting the HHV of biochar from proximate analysis results.

Model	Components	EF
M6	C% and O%	0.943
M7	Fixed C% and Ash%	0.951

7.2.4 Comparing new models with literature equations

The results of ultimate and proximate analysis (dry mass basis), obtained from analysis of WP and SP biochar (Chapter 5), were incorporated into E1 – E8 to estimate the HHV of biochar. The EF of these equations was then assessed and compared to the EF of M6 and M7, as seen in Table 7-6.

Table 7-6: Comparison of regression equations taken from literature with new models for predicting biochar HHV.

Equation / Model	Components	EF
E1	C%, H%, N% and O%	0.823
E2	C% and H%	0.185
E3	C%, H% and O%	0.232
E4	FC%	0.745
E5	VM% and Ash%	0.942
E6	FC%, VM% and Ash%	0.885
E7	FC% and VM%	-1.671
E8	FC%, VM% and Ash%	-3.943
M6	C% and O%	0.943
M7	Ash% and FC %	0.951

By assessing a systematic set of biochar samples, two new models were derived from the results of ultimate analysis and proximate analysis which demonstrated a strong fit of predicted biochar HHV with the observed heating value of the same biochar samples. Compared to the regression equations taken from literature, the EF of M6 and M7 were generally substantially higher, especially in the case of E2, E3, E7 and E8. While the EF can have a maximum number of 1 it can also be a negative number as seen for E7 and E8. If the EF is less than zero the model-predicted values were worse than simply using the observed mean. As EF also assesses strength of linearity, a negative value can also indicate that a non-linear model may be the preferred option for predicting HHV.

7.2.5 **Gas HHV**

In Chapter 5 and 6 the gas product was collected during each pyrolysis run and analysed for composition. The overall composition of the pyrolysis gas mixture, volume of gas collected and HHV of the individual gas species were used to calculate the HHV of the product gas. However it was the aim of this section to derive a simpler equation for predicting the HHV of the gas stream based on the production conditions of the pyrolysis system and the feedstock composition.

From the "Best Subsets" analysis (Figure 7-11) several models showed similar values for r^2 adjusted, but with varying numbers of variables.

Vars	R-Sq	R-Sq(adj)	Mallows Cp	S	Heat Treatment	Heating Rate	Residence Time	Feed Flow	Cooling Gas	Heating Coil	Feed Size	Feedstock Lignin Content	Feedstock Ash Content %
1	77.9	77.5	26.8	1.6822	X								
1	7.3	5.7	287.9	3.4452		X							
2	83.5	82.9	8.2	1.4681	X	X							
2	79.4	78.7	23.1	1.6371	X			X					
3	85.0	84.2	4.5	1.4110	X	X		X					
3	83.6	82.7	9.8	1.4762	X	X	X						
4	85.1	84.0	6.1	1.4185	X	X	X	X					
4	85.0	83.9	6.4	1.4221	X	X		X					X
5	85.7	84.4	5.8	1.4026	X	X		X		X			X
5	85.6	84.2	6.4	1.4101	X	X		X	X				X
6	85.9	84.3	7.0	1.4046	X	X		X	X		X		X
6	85.9	84.2	7.3	1.4089	X	X	X	X		X			X
7	86.3	84.4	7.8	1.4020	X	X		X	X	X	X		X
7	86.1	84.2	8.4	1.4101	X	X	X	X	X		X		X
8	86.5	84.3	9.0	1.4046	X	X	X	X	X	X	X		X

Figure 7-11: Best subset procedure results for determining the most suitable model for predicting gas HHV using production conditions and feedstock composition. Screen shot of statistical analysis taken from Minitab 16.

One model (M8) demonstrated a good fit (r^2 adj = 84.2) while only containing the three variables of HTT, heating rate and flow rate as seen in Figure 7-12. While this model contained no feedstock properties, the inclusion of feedstock composition into the model only causes a slight improvement in model fit (r^2 adj = 84.4) which was most likely down to the increased number of variables. However the presence of feedstock C% and hemicellulose in the model (as seen in Figure 7-13) was not statistically significant and so was not considered any further.

```
The regression equation is
Gas HHV = - 5.37 + 0.0226 Temperature + 0.0224 Heating Rate + 2.07 Flow Rate


Predictor         Coef   SE Coef      T      P
Constant       -5.3662    0.7659  -7.01  0.000
Temperature   0.022629  0.001354  16.71  0.000
Heating Rate  0.022437  0.004969   4.52  0.000
Flow Rate       2.0702    0.8728   2.37  0.021


S = 1.41098   R-Sq = 85.0%   R-Sq(adj) = 84.2%


Analysis of Variance

Source          DF      SS      MS       F      P
Regression       3  620.33  206.78  103.86  0.000
Residual Error  55  109.50    1.99
Total           58  729.83
```

Figure 7-12: Linear regression model for predicting gas HHV containing the variables of HTT, heating rate and carrier gas flow rate. Screen shot of statistical analysis taken from Minitab 16.

```
The regression equation is
Gas HHV = - 16.6 + 0.0225 Temperature + 0.0211 Heating Rate + 2.07 Flow Rate
          + 0.0572 Hemicellulose + 0.200 Feedstock C%


Predictor          Coef   SE Coef      T      P
Constant        -16.605     6.934  -2.39  0.020
Temperature    0.022536  0.001348  16.72  0.000
Heating Rate   0.021064  0.005027   4.19  0.000
Flow Rate        2.0702    0.8676   2.39  0.021
Hemicellulose   0.05715   0.03605   1.59  0.119
Feedstock C%     0.1997    0.1227   1.63  0.110


S = 1.40260   R-Sq = 85.7%   R-Sq(adj) = 84.4%


Analysis of Variance

Source          DF      SS      MS      F      P
Regression       5  625.56  125.11  63.60  0.000
Residual Error  53  104.27    1.97
Total           58  729.83
```

Figure 7-13: Linear regression model for predicting gas HHV containing the variables of HTT, heating rate, carrier gas flow rate, hemicellulose and feedstock C content. Screen shot of statistical analysis taken from Minitab 16.

While the 'Best Subsets' approached showed the potential for a strong fit of the predicted values against the observed values, the EF of M8 was calculate to be 0.85, as shown in Table 7-7. In an attempt to improve the modelling efficiency, the gas compositions measured after pyrolysis were considered as variables in the best fit model (Figure 7-14). By following this approach, a new linear regression model (Figure 7-15), referred to as M9, was produced which consisted of HTT, H_2, CH_4, C_2H_6 and CO.

Vars	R-Sq	R-Sq(adj)	Mallows Cp	S	Heat Rate	Heat Input	Reactor Temperature	Heat Transfer	Feed Flow	Feedstock Lignin	Feedstock Cellulose	Feedstock Ash	Feedstock Moisture	Gas CO2 %	Gas CH4 %	Gas H2 %	Gas CO %
1	91.9	91.7	161.2	1.0209													X
1	77.9	77.5	532.0	1.6822	X												
2	96.7	96.6	33.4	0.65123											X		X
2	94.5	94.3	92.0	0.84340										X		X	
3	97.5	97.4	15.6	0.57670											X		X X
3	97.3	97.1	21.2	0.60050											X	X	X
4	97.7	97.5	13.0	0.56155										X		X	X X
4	97.7	97.5	13.4	0.56351										X	X	X	X
5	98.1	97.9	4.5	0.51689	X									X	X	X	X
5	98.0	97.9	5.1	0.51986	X									X		X	X X
6	98.1	97.9	4.4	0.51076	X								X	X	X	X	X
6	98.1	97.9	5.0	0.51403	X	X								X	X	X	X
7	98.2	98.0	4.9	0.50780	X		X						X	X	X	X	X
7	98.2	97.9	5.0	0.50839	X	X							X	X	X	X	X
8	98.2	98.0	5.5	0.50550	X	X		X					X	X	X	X	X
8	98.2	97.9	6.2	0.50912	X			X		X			X	X	X	X	X
9	98.3	97.9	7.2	0.50882	X	X		X		X			X	X	X	X	X
9	98.3	97.9	7.2	0.50909	X	X	X	X					X	X	X	X	X
10	98.3	97.9	8.8	0.51186	X			X	X	X	X		X	X	X	X	X
10	98.3	97.9	9.0	0.51291	X	X	X	X		X			X	X	X	X	X
11	98.3	97.9	10.5	0.51570	X			X	X	X	X	X	X	X	X	X	X X
11	98.3	97.9	10.5	0.51572	X		X	X	X	X	X	X	X	X	X	X	X
12	98.3	97.9	12.2	0.51939	X		X	X	X	X	X	X	X	X	X	X	X X
12	98.3	97.9	12.3	0.51999	X	X	X	X	X	X	X	X	X	X	X	X	X
13	98.3	97.8	14.0	0.52419	X	X	X	X	X	X	X	X	X	X	X	X	X X

Figure 7-14: Best subset procedure results for determining the most suitable model for predicting gas HHV using production conditions, feedstock and gas composition. Screen shot of statistical analysis taken from Minitab 16.

```
The regression equation is
Gas HHV = 0.549 - 0.00439 Temperature + 0.264 H2 % + 0.0868 CO % + 0.348 CH4 %
          + 0.519 C2H6 %


Predictor         Coef   SE Coef      T      P
Constant        0.5492    0.5133   1.07  0.289
Temperature  -0.004390  0.001313  -3.34  0.002
H2 %           0.26376   0.01400  18.84  0.000
CO %           0.08675   0.01417   6.12  0.000
CH4 %          0.34834   0.03231  10.78  0.000
C2H6 %          0.5194    0.1239   4.19  0.000


S = 0.516892   R-Sq = 98.1%   R-Sq(adj) = 97.9%


Analysis of Variance

Source          DF      SS      MS       F      P
Regression       5  715.67  143.13  535.73  0.000
Residual Error  53   14.16    0.27
Total           58  729.83
```

Figure 7-15: Linear regression model for predicting gas HHV from the variables of HTT, H_2, CO, CH_4 and C_2H_6. Screen shot of statistical analysis taken from Minitab 16.

A model using CO_2 instead of CO showed an identical r^2 adj value but a higher Mallow's C-p value so M9 was preferred. The EF of M9 was included in Table 7-7 alongside that of M8 and showed an improvement in predicting gas HHV. However the observed gas HHV was initially calculated using the gas composition measured after pyrolysis as well as other gas related measurements, so the strong predictive capability of M9 is not surprising. Nevertheless the calculation of gas HHV, used in Chapter 5 and 6, has been greatly simplified through the removal of factors such as total gas volume, individual HHV of gas species as well as additional measurements detailed in section 2.4.3.3.

Table 7-7: Comparison of the model efficiencies for predicting the HHV of the pyrolysis gas stream.

Model	Components	EF
M8	HTT, heating rate and carrier gas flow rate	0.849
M9	HTT, H_2, CH_4, C_2H_6 and CO	0.981

7.3 Conclusion

Through compiling one large data set it was possible to carry out statistical analysis on the overall results of the thesis to look for statistical relationships between the production conditions and the final biochar properties. These relationships led to the generation of linear regression equations which could be applied to give strong predictions into biochar properties such as stable-C concentration, stable-C yield and biochar HHV.

Through regression equations, biochar stable-C yield could be predicted by using the intended pyrolysis conditions prior to biochar production in addition to the biomass components of cellulose, hemicellulose and lignin. The multiplication factor before each variable in the regression model can also be used in conjunction with the range of the individual variable to demonstrate the contribution of each variable to the total output. Being able to estimate the C storage potential of biochar could be applied as an initial screening tool to identify new production conditions or feedstock types which could produce biochar with a high stable-C yield. However to be able to predict the stable-C yield from new process conditions and feedstock type, the new variables must be part of the regression model; and have their values fall within the range used in the initial regression equation. This limits the current application of the model however continued investigations can expand the range of the model and strengthen its predictive capability. The strength of the model would then lie in reducing the knowledge gaps between the already investigated variables, while also providing a rapid assessment tool for determining biochar properties prior to large scale production. This is the main drive for developing additional regression models for predicting the heating value of biochar and pyrolysis gas. Biochar can be used as a fuel source and the heating value is an important attribute, especially when considering fast pyrolysis and gasification operations where biochar is not the desired product. Using the composition of biochar as part of regression equations to calculate the HHV of biochar could reduce the need for additional analysis using highly specialised and expensive equipment (bomb calorimetry and TGA); however the models can only provide estimations of the final value. Throughout this PhD the

extent of analysis has been limited through the amount of biochar produced during pyrolysis, and therefore these linear regression models could provide an insight into additional biochar properties while conserving the biochar product for other more important analytical tools.

Chapter 8. **Discussion**

This discussion brings together the findings from Chapters 3 – 7 to address the key objectives listed in Chapter 1, especially Objective 5 to understand the degree of control the process conditions can have over biochar properties to assess the potential for bespoke biochar. Through the production and analysis of a systematic set of biochar samples, this thesis has aimed to assess the influence production conditions have on the C sequestration potential (Chapters 3, 4, 5 and 6) and soil amendment properties of biochar (Chapter 3 and 4) in an attempt to refine the pyrolysis process, improving the potential for the future production of bespoke biochar. Furthermore, this thesis considered the importance of investigating how changing the pyrolysis conditions could impact the energy content of pyrolysis products (Chapters 5 and 6) and the implications this might have on the ideal parameters for biochar production (Chapters 5 and 6). The use of a systematic set of biochar samples, as opposed to a random sample set, can be applied to effectively identify and explain relationships between production and final properties. This could then be used to potentially create models of biochar function (Chapter 7) with different feedstock / production parameters.

8.1 **Background**

In the early 1920s there was a shift from the use of biomass resources for energy generation to that of fossil fuels, as these became more available and cheaper. However, recently, growing environmental concerns have started to swing the momentum back towards renewable sources, including biomass, as the preferred option for mankind's energy, chemical and agronomical needs (Spokas *et al.*, 2012). The atmospheric carbon level is rapidly approaching what the Intergovernmental Panel on Climate Change (IPCC) have dubbed a 'tipping point' beyond which changes to our climate may become catastrophic and irreversible (Pacala & Socolow, 2004; Mathews, 2008; IPCC, 2014). The atmospheric concentration of CO_2 can only be stabilized if the global (net) CO_2 emissions peak and then decline towards zero in the long term. Simply improving the energy efficiency of fossil power plants or

shifting the focus to natural gas rather than coal will not be sufficient to achieve CO_2 stabilisation (IPCC, 2014). Therefore the focus on reducing CO_2 emissions through alternative energy sources and CCS solutions has become clearly visible across the world. Of the many different proposed technologies, biochar production is one of a few carbon-negative alternatives that can effectively reduce CO_2 concentration in the atmosphere. This is achieved through pyrolysis which stabilises the majority of C, removed from the atmosphere though photosynthesis, as biochar in soil for hundreds of years. For biochar to be the preferable option over biofuel production the carbon stabilization needs to be combined with the generation of heat and power through liquid and gas co-products (Sohi, 2012). At least one-third of terrestrial NPP is now believed to be managed by humans (Running, 2012). By diverting a small percentage of these global biomass resources into biochar production, a significant contribution could be made to achieving a reduction in atmospheric CO_2 levels while providing an alternative energy source to fossil fuels. Matovic (2011) proposed that if 10 % of the world biomass NPP was converted into 50 % charcoal and 30 % energy from volatiles, it would sequester approximately 4.8 GtC $year^{-1}$. This would generate a C abatement value equivalent to almost 5 wedges in the carbon and climate stabilisation triangle (Pacala & Socolow, 2004).

Although biochar research is in its infancy, much has already been characterised and discovered with respect to production and application. However, a better understanding of how to control the soil enhancing benefits of biochar is needed for biochar to compete with the growing demand for energy through biomass combustion. This is where potential trade-offs between the soil enhancing and C mitigation benefits of biochar and the biofuel potential of pyrolysis may occur. Jeffery *et al.* (2013) used the five most often reported benefits of biochar (soil fertility, climate change, waste disposal, biofuels and soil remediation) to conceptualise important examples of biochar trade-offs, in particular C sequestration potential vs. enhanced agronomic properties and C sequestration vs. energy production. Without financial incentives for carbon abatement (e.g. carbon markets), the application of biochar in soil has to economically feasible (Sohi, 2012). While the

mechanisms by which biochar influences soil fertility are not yet fully understood, literature has shown that biochar can affect the concentration of soil organic carbon (SOC), soil pH, water holding capacity, CEC and soil microbial ecology (Lehmann *et al.*, 2006; Liang *et al.*, 2006; Atkinson *et al.*, 2010; Sohi *et al.*, 2010; Van Zwieten *et al.*, 2010; Jeffery *et al.*, 2011; Spokas *et al.*, 2012; Biederman & Harpole, 2013; Liu *et al.*, 2013; Ronsse *et al.*, 2013). Due to the number of different process parameters (equipment, process, temperature etc.), along with the large variety of potentially available feedstock, there is a countless number of biochar types that can be produced and experimented with (Enders *et al.*, 2012; Jeffery *et al.*, 2013; Ronsse *et al.*, 2013). The large number of options makes it difficult for any real advancement in controlling biochar's environmental performance because of inconsistent results. Therefore it is important to develop a mechanistic understanding to allow for the assessment of potential trade-offs needed before large-scale application of biochar can be promoted (Jeffery *et al.*, 2013). A number of studies have extensively covered the physicochemical properties of biochar (Williams & Besler, 1996; Antal & Grønli, 2003; Demirbas, 2006b; Shackley & Sohi, 2010; Enders *et al.*, 2012; Angin, 2013), however the functional properties of biochar, which determine its effectiveness and response in soil, are under researched and are of more importance to targeted biochar application.

Increasing the yield of biochar can be effected by applying less severe pyrolysis conditions, and so biochar production has been associated with a loss of heat/power generation potential due to the reduced yields of liquid and gas co-products (Antal & Grønli, 2003; Demirbas, 2004; Demiral & Ayan, 2011; Hossain *et al.*, 2011; Chen *et al.*, 2012; Manyà, 2012; Angin, 2013; Mašek *et al.*, 2013b). The preferential production of biochar therefore needs to be justified when compared to alternative energy technologies such as fast pyrolysis and gasification geared towards maximising biofuel production (Pratt & Moran, 2010; Bridgwater, 2012). However, very little is actually known about the product energy distribution of slow pyrolysis and how altering pyrolysis conditions could influence the final energy output of the system. Understanding the influence that pyrolysis conditions have on energy

distribution and biochar functional properties as well as the trade-off between these benefits, is essential to not only refining the pyrolysis process to improve the consistency of biochar quality and environmental performance, but also for assessing the overall C mitigation potential of pyrolysis.

8.2 Synergies and trade-offs between biochar properties

Biochar literature can be segregated into different categories focusing on the agronomic benefit of biochar (stability, soil properties, soil nutrients, plant responses, contaminants, trace gases etc.), the production and characterisation of biochar, and the socio-economics of biochar (modelling, LCA etc.) (Gurwick *et al.*, 2013). Gurwick *et al.* (2013) use a systematic review of 311 peer-reviewed biochar articles, to show that most commonly, literature describes the production processes of biochar and/or the characterisation of its physical or chemical properties. Investigations into the agronomic value of biochar were also heavily featured, while the large majority of the collected articles focused on the laboratory analysis of biochar, with very few investigating field response. Improving the understanding of how production conditions can fully influence the agronomic and economic benefits of biochar is vital to improving the commercial potential of biochar. The ability of biochar to improve soil quality and crop production has been attributed to several factors, including increased soil pH, retention of soil nutrients, improved water retention, toxin neutralisation, habitat for microbial communities, improved N fertilizer-use efficiency and reduced soil strength (Lehmann *et al.*, 2006; Chan & Xu, 2009; Van Zwieten *et al.*, 2010; Zimmerman *et al.*, 2011; Biederman & Harpole, 2013; Liu *et al.*, 2013). Identifying the combination of feedstock and pyrolysis conditions required to produce biochar with characteristics aimed at addressing soil constraints has been identified as a topic lacking research. However, due to the number of production conditions which can be altered during pyrolysis and the variation these conditions can have on a multitude of biochar properties (chemical composition, surface area, pore volume, pH, stability etc.), attempting to maximise each potential functional property may not be achievable. This is where potential trade-offs

between biochar's multiple potential applications (soil enhancement, C sequestration, energy generation etc.) may occur. Through considering these trade-offs, the pyrolysis process could be set-up to maximise a particular feature and/or minimise trade-offs.

There is a large array of production variables (type of pyrolyzers, scale of pyrolysis, starting material, temperature etc.) which can be changed during pyrolysis, leading to a lack of consistency between biochar studies on the agronomic response of biochar. Therefore studying how several production conditions (HTT, heating rate, residence time and carrier gas flow rate) can influence biochar functional properties can begin to narrow down the large variety of biochar and generate more consistency between studies. The impact of a number of production conditions on the long term environmental stability of biochar was addressed in Chapters 3, 4, 5 and Appendix 3, while the short term degradation was also considered in Chapters 4 and 5. In addition to stability, other important functional properties such as the pH of biochar, concentration of extractable nutrients, and biochar CEC, were reported in Chapter 4; and the enhancement of these properties was considered alongside that of C stability. While the focus here is on the trade-offs between C sequestration, soil enhancing properties and energy generation it is important to acknowledge that there are other potential benefits (e.g. water retention, decreased GHG emission etc.) not debated within this thesis.

8.2.1 Maximizing the functional properties of biochar

8.2.1.1 Biochar long term stability

The results of proximate analysis (fixed C) and ultimate analysis (elemental ratios) have extensively been used to assess the C stability of biochar. However these measurements do not give a good indication of the treatment conditions biochar could go through once applied to soil. This has led to the development of a new analytical tool using direct oxidation to improve the assessment of biochar's C stability. The HTT was consistently identified in Chapters 3, 4, 5 and Appendix 2 as the defining variable for determining the concentration of stable-C present within biochar. The results in these chapters all agree that by increasing the HTT of

pyrolysis the stable-C concentration would also increase, indicating improved biochar stability with HTT. More importantly, when considering the efficiency of the conversion of feedstock C to stable-C (stable-C yield), increasing the HTT continued to show improved C stabilisation, reported in Chapters 3, 4 and 5 (Appendix 3 was excluded as feedstock C data was not available). This important finding then indicates that it is not the amount of biochar which is important to sequestering C but the overall yield of the stable fraction of biochar C.

Overall, the heating rate selection in the range investigated showed no statistically significant influence on the stability of biochar; however this could be due to the dominating effect that HTT has over biochar properties at elevated temperatures. When pyrolysis is performed at 350^{o}C, the stable-C concentration of biochar was consistently lower when using the higher heating rate, although this difference was not deemed to be statistically significant. The effect of residence time and carrier gas flow rate on biochar stability was only investigated within Chapter 5, and while residence time demonstrated no statistical effect on either the concentration or yield of stable-C, an increasing carrier gas flow rate decreased the yield of stable-C due to minimising the formation of secondary char.

Although in Chapter 3 the feedstock was not deemed to influence the final biochar stable-C concentration, it did exhibit an impact on the more critical measurement of stable-C yield. Feedstock type also showed increased impact in Chapter 4 with the selection influencing both stable-C content and yield. Combining the results for biochar stability from Chapters 3, 4 and 5 led to an overall significant effect of feedstock selection on the final yield of stored C in biochar. The highest stable-C yields were seen for biochar produced from grass/straw-based compared to wood-based biochar. Appendix 3 covered a wider range of different biochar types and the stable-C concentration of biochar produced from woody biomass was consistently higher than that of biochar produced from manure/waste material at the same HTT. The stable-C yield for these samples was not calculated due to a lack of data on feedstock C concentration. The lower stable-C concentration of manure/waste biochar could be the result of larger concentrations of ash and lower C content

present in waste biomass compared to that of straw material, thus limiting the stable-C fraction of biochar. The difference could also be due to the composition of the ash fraction affecting catalytic reactions and secondary char formation during pyrolysis as the composition of manure/waste materials would differ considerably to that of virgin straw biomass.

In summary, increasing the severity of pyrolysis has clearly shown an improvement in the C sequestration ability of biochar, which can then open the door to advance the economic and environmental benefits achieved at high HTT such as improved energy output (Chapter 5 and 6), and further development of physical properties which may not occur at lower temperatures. It should also be noted that the assessment of biochar stability was carried out on powdered biochar to remove any physical protection which would ultimately increase the recalcitrance of biochar when applied to soil.

8.2.1.2 Short term biochar degradation

After low temperature pyrolysis, biochar may contain an unconverted or partially converted biomass fraction, known as labile-C, which is rapidly mineralized on addition to soil. While the long term stability of biochar is vital to understanding the C sequestration potential of pyrolysis, it is also important to assess the proportion of biochar which can be rapidly degradable. The results of Chapter 4 and 5 both confirmed the significant influence that HTT and feedstock have on the labile-C concentration of biochar. Increasing the HTT of pyrolysis showed a considerable drop in the concentration as well as yield of labile-C present within biochar. Straw-based biochar contained much higher concentrations of labile-C (WS = 0.83 $\pm$ 0.27 %, WSP = 0.99 $\pm$ 0.32 %) compared to woody biochar (PC = 0.19 $\pm$ 0.07 %) when produced at HTT below 450^{o}C. The high labile-C concentration in straw biochar could be attributed to the high ash concentration leading to formation of easily degradable carbonates (Enders *et al.*, 2012). However, as pyrolysis HTT was increased, the difference in biochar labile-C concentration between feedstock types was reduced. This meant that at 650^{o}C the feedstock selection was no longer deemed to be statistically significant (Chapter 4 and 5). The chosen heating rate (Chapter 4),

residence time (Chapter 5) and carrier gas flow rate (Chapter 5) showed no effect (for the ranges investigated) on the concentration or yield of labile-C. As the fraction of feedstock C associated with labile-C is relatively small especially at 650^{o}C (< 0.1 %), the amount of C being emitted is extremely small and should generally have a negligible effect on C sequestration. However the assessment of labile-C focuses on the CO_2 emissions from biochar and does not consider additional reactions caused by the presence of biochar in soil such as mineralisation of SOM and stabilisation with soil minerals. Biochar has been reported to cause the priming of SOM over short periods of time (Zimmerman *et al.*, 2011); however these losses might be negligible in many cases due to the loss of native SOM being smaller than the C gained following biochar application to soil (Woolf & Lehmann, 2012).

From the work carried out in this thesis it was seen that by performing pyrolysis at higher temperatures ($\geq$ 550^{o}C), the amount of biochar C with long term stability (> 100 years) increased, while also minimising the fraction of biochar C which could undergo rapid mineralisation (2 weeks) within the environment. These measurements do not account for the total C present within biochar and so indicate a third fraction of intermediate C stability (Int-C) ranging from 2 weeks to 100 years. The consideration of this third fraction of biochar stability is important for better understanding the degree of C storage possible through biochar production. However the degradation of biochar (short or long term) in the environment may be found to be lower than under laboratory conditions because of less favourable treatment conditions, or perhaps higher due to stimulatory reactions occurring within soil. Either way, assessing biochar for stable-C and labile-C content can help to rapidly screen fresh samples and provide strong indications of environmental stability of biochar prior to its application to soil.

8.2.1.3 **Biochar pH**

The pH of biochar (Chapter 4) was clearly increased when increasing the severity of pyrolysis, due to the release of acidic volatile material and increased concentration of non-pyrolyzed inorganic elements at elevated temperatures. Biochar with an alkaline pH can cause a liming effect within soil and therefore raise soil pH, leading to

improvements in soil fertility, especially in acidic soils. However it should also be considered that when applying biochar to soil it is important to not cause additional problems while trying to improve the targeted deficiency. Applying biochar with too high a pH could cause problems in certain soils (Chan & Xu, 2009; Rajkovich *et al.*, 2011); therefore the pyrolysis process can be engineered by employing alternative feedstock (e.g. low ash concentration) or alternative production conditions to produce biochar with lower alkalinity. For determining the ideal pH for biochar, the location and soil properties must be considered beforehand.

8.2.1.4 Extractable nutrients in biochar

Chapter 4 was entirely focused on determining potential relationships between production conditions and the functional properties of biochar. While both labile-C and pH were both clearly influenced by HTT, the same cannot be said for the concentration of extractable nutrients and CEC of biochar. Biochar nutrients are mainly located within the feedstock ash, and are largely retained in the final biochar product so feedstock was deemed to be the determining factor in the biochar nutrient concentration.

While high HTT ($\geq 550^{o}C$) has consistently shown a high C storage potential, high alkalinity, low labile-C concentration as well as high values of CEC, the concentrations of available Ca, K, Mg, Na and P generally peaked from biochar produced at $450^{o}C$ at both heating rates. The release of nutrients was hindered by pyrolysis HTT at elevated temperatures because of modifications to biochar structure (structure re-ordering, pore blockage and surface area) and composition (increased aromatic C, melting or fusing of ash content). The application of a higher heating rate also produced different results depending on the concentration of ash present within the biochar. As seen in Chapter 4, to maintain high nutrient contents and availability of these nutrients, the preferred temperature of pyrolysis (over the range investigated) would be between $450^{o}C$ – $550^{o}C$. This also coincided with the proposed range between which the CEC of biochar generally reached its highest value.

8.2.1.5 **Predicting the stability of biochar**

Biochar's agronomic value is poorly understood, which in part is due to the inability to predict its impact in soil. Before field-scale application of biochar can be recognised, it is necessary for the positive and negative effects of biochar to be properly understood through improved predictability and reproducibility of biochar properties (Shackley *et al.*, 2011). Therefore through analysing a systematic set of biochar samples, statistical models were designed, as seen in Chapter 7, enabling prediction of biochar properties and its performance as a function of feedstock, processing conditions, and application-specific parameters.

Statistical models were developed, based on linear regression, which could be applied to give strong predictions for the stable C concentration and stable-C yield (both using 67 observations). These models were constructed from statistical relationships between the measured properties of biochar, the production conditions (HTT, heating rate, residence time and carrier gas flow rate) and feedstock composition (cellulose, hemicellulose, lignin, feedstock ash content and total feedstock C content). The simplest model for predicting stable-C concentration contained the four variables of HTT, cellulose, hemicellulose and lignin content, demonstrating the dominating influence of feedstock selection and pyrolysis temperature. However the best suited model for predicting the stable-C yield of biochar only contained the feedstock property of ash concentration in addition to HTT, heating rate and carrier gas flow rate. This demonstrated that when predicting the overall yield of stable-C, the feedstock components of cellulose, hemicellulose and lignin were not needed. Other models were designed which produced a higher EF, but these models also contained a higher number of variables and therefore increased the model complexity. The ability to predict biochar stability could be applied as a screening step prior to pyrolysis for new production conditions or feedstock, as long as the new variables are within the range of the current model. Further studies using new process conditions would aid in expanding the model's limitations while also help to improve the strength of the prediction.

8.2.2 Enhancing soil fertility or sequestrating C

When considering the process conditions needed for improving biochar's soil amendment properties, trade-offs between the soil-enhancing benefits and long term stability of biochar could have a defining impact on the selection of pyrolysis conditions. The consideration of production conditions should be aimed at finding a balance to minimize the potential trade-offs rather than maximizing one property. However determining the balance between nutrient composition and C mitigation may prove extremely difficult due to the large variability in biochar and feedstock composition, especially where nutrient content is concerned (Chan & Xu, 2009).

Biochar produced at higher temperatures was deemed to be more effective at promoting aboveground productivity (Biederman & Harpole, 2013; Liu *et al.*, 2013). At higher temperatures, biochar is found to be alkaline in nature and contain less biologically active volatile material which could limit plant growth. High temperature biochar also has increased stability from chemical and biological decomposition, and would therefore better fulfil the function of sequestering C while also increasing SOC (Novak & Busscher, 2013). However the condensed aromatic structures commonly associated with recalcitrant biochar may contain fewer ion exchange functional groups and so limit the retention of soil nutrients (Novak *et al.*, 2009). This is one indication of where improving both the C sequestration potential and soil enhancing benefit of biochar may not be possible. Further tests would be needed to compare the importance and duration of plant-available nutrients over other functional properties, since maximizing one property might deliver a better response for improving soil fertility than other properties. Although applying a HTT $< 550^{o}C$ appeared to produce biochar with a higher concentration of extractable nutrients, Liu *et al.* (2013) reported that pyrolysis at higher pyrolysis temperatures significantly increased crop productivity owing to the liming effect caused by increasing biochar pH with HTT. Biochar produced from feedstock containing a high nutrient concentration (poultry biomass) has been shown to increase crop productivity to a higher extent compared to feedstock with lower nutrient content (woody biomass) (Jeffery *et al.*, 2011). However biochar produced from poultry like

material has also demonstrated lower stability compared to woody biochar (Enders *et al.*, 2012; Singh *et al.*, 2012). Therefore, although a lower HTT would benefit the plant availability of nutrients and CEC of biochar, the more important properties might be those of pH or C stability which peak under more intense pyrolysis conditions. The effects of liming and direct nutrient addition are likely to be short-term since the nutrients are used or leached from the system, while other effects of biochar on soil could be more endurable but slower to develop such as CEC (Jeffery *et al.*, 2013). With time the oxidation of biochar may lead to developments in functional properties, especially increased CEC, and thus improve the soil-enhancing ability of biochar. However the same process can lead to a loss of C, thereby reducing the C sequestration potential of biochar (Jeffery *et al.*, 2013). Therefore further consideration would be needed for the overall importance of the short-lived soil enhancing features of biochar compared to those which would last decades or longer.

As previously seen within Chapter 4, the task of trying to maximise both the soil enhancing and C sequestration benefits of biochar is not a simple one. The desired properties of biochar might not necessarily be engineered to attempt to maximise both of these benefits, but rather be designed to address constraints in a specific location. Biochar does not refer to one singular product but rather a range of products. One type of biochar will not be able to solve all soil quality problems since each desired location will undoubtedly have unique quality issues (Novak *et al.*, 2009). If biochar has a benign influence on soil fertility, then at the very least that type of biochar might be appropriate for long-term C storage. However, if the goal is for improving soil productivity, then applying a biochar with definitive chemical and physical properties known to change soil properties may be more important. Alternatively, blending together different types of biochar or biomass prior to pyrolysis could produce a hybrid product with designed characteristics to improve multiple soil properties (Novak & Busscher, 2013; Novak *et al.*, 2014). For example, biochar could be made from a combination of wood and poultry litter or manure to design a biochar product with high C sequestration potential while also providing

additional benefits such as added nutrients, improved soil water storage, pH, and containing high C,N and P concentrations (Novak & Busscher, 2013; Novak *et al.*, 2014). This concept could further develop the 'designer biochar' market to improve the minimisation of the potential trade-offs between carbon sequestration and soil enhancement. If studies continue to show biochar to have negligible or positive effects on soil, then its future success and focused production may depend on the trade-off between a high-cost bespoke biochar and a cheaper more readily available product.

8.2.3 The carbon-energy balance

Slow pyrolysis technology favours biochar production and is therefore best able to take advantage of the carbon sequestration and soil enhancing benefits that improve the potential for carbon negative biofuels. Using biomass for production of biochar rather than biofuel is associated with a loss of heat/power generation potential (Gaunt & Lehmann, 2008), and therefore the C mitigation potential of biochar is considered to be achieved at a cost of diminished biofuel output (Jeffery *et al.*, 2013). Fast pyrolysis optimised for biofuel production has an energy output approximately 30 % higher than that of slow pyrolysis, favouring biochar production (Gaunt & Lehmann, 2008). Therefore the production of biochar needs to be justified by offering significant other benefits such as soil enhancement and C abatement, offsetting the loss in heat/power generation.

LCA has been used to show that when the potential soil benefits of biochar (reduced GHG emissions, increased crop productivity etc.) are included, biochar production could be favourable compared to the direct combustion of biomass (Hammond *et al.*, 2011). However, increasing biochar production will always decrease the energy output within the same system (Gaunt & Lehmann, 2008) and therein lies an essential trade-off between biochar production and the energy output of pyrolysis, leading to competition in policy objectives between bioenergy vs. C abatement (Sohi, 2012). The C mitigation impact of biochar has been estimated to be larger than if the same biomass was fully combusted for energy (Woolf *et al.*, 2010), thus the argument is not for or against biochar production but instead under which process

conditions the energy output of a biochar production system can be maximised without great sacrifice of C mitigation.

Very little is known with regard to the trade-off between the energy contained within pyrolysis co-products and the C sequestration potential of biochar, leading to a need for further work on comparing energy pathways with the C abatement of biochar to allow for quantification of this trade-off (Jeffery *et al.*, 2013). Hence the impact of pyrolysis conditions on the energy distribution between solid, liquid and gas co-products, as well as how varying these conditions affected the C sequestration potential of biochar, was investigated in Chapter 5. Additionally the energy content of pyrolysis gas was assessed in Chapter 6, to explore the possibility that the energy required to maintain the pyrolysis process could be solely provided by the gas stream, thus increasing the availability of liquid and char products.

8.2.3.1 Energy distribution

The results in Chapter 5 once again showed the high impact of HTT on biochar properties, with specific focus on the distribution of the total feedstock energy content amongst the pyrolysis co-products. The overall energy balance of the pyrolysis products was determined by expressing the individual energy content of the char, liquid and gas fractions as a proportion of the feedstock energy content. As the HTT was increased, the energy balance shifted to the liquid and gas products, through the release of volatile matter, thus decreasing the overall contribution of biochar to the total energy balance. This shift was a result of the combined effect of higher HTT increasing the HHV of pyrolysis co-products while also decreasing the char yield and consequent increasing liquid and gas fractions. Although the char and liquid heating values were not covered in Chapter 6, the gas energy content was also clearly increased by executing pyrolysis at a higher HTT. The influence that feedstock and carrier gas flow rate had on the product distribution and heating values of co-products was also exhibited in the final energy distribution amongst products. A higher carrier gas flow rate was seen to raise the contribution of the gas stream to total energy, due to the increased gas yield and gas HHV also associated with higher carrier gas flow rates. Furthermore, the energy fraction associated with biochar was

larger for WP biochar compared to SP, potentially due to the high ash concentration of SP. Ronsse *et al.* (2013) proposed that the presence of ash can lead to a 'dilution' effect of the char HHV. Overall, HTT was the dominating variable when determining the distribution of total feedstock energy between the solid, liquid and gas co-products, while feedstock and carrier gas flow rate were also influential, but only at low HTT.

8.2.3.2 **Carbon emissions**

As previous discussed in Chapter 5, the choice of HTT can shift the product mass distribution which then has a direct effect on the amount of C distribution among the char, liquid and gas fractions. By increasing the HTT, C is released from biochar, in the form of volatile matter and is collected in the liquid and gas products. While the char mass may have decreased with increasing HTT, Chapter 5 demonstrated that the stable-C yield and therefore the mass of stable-C actually increased with temperature. The C contained within the liquid and gas fractions can be regarded as emitted C, while biochar C can be divided into stable-C, labile-C (also emitted C) and intermediate C (Int-C). The intermediate C then influences the amount of C which is emitted or stored depending on whether or not the intermediate C is stable or easily degradable. At elevated HTT the vast majority of biochar C is highly stable; therefore the Int-C fraction has little impact on carbon emissions. This further iterates the added advantage of performing pyrolysis at higher HTT for improving the C storage ability of biochar. At low HTT the majority of energy resides within the char fraction and thus is unavailable for heat/ power generation. That, coupled with the lower concentrations of stable-C and larger amounts of labile-C and Int-C, resulted in low temperature pyrolysis releasing a much higher amount of C per MJ of chemical energy produced compared to pyrolysis at 650^{o}C (Chapter 5). The difference between emitted C and stored C could therefore influence the feedstock selection. Pyrolysis of SP biomass consistently showed lower emitted C per MJ of chemical energy produced, due to a higher combined energy content of the liquid and gas fractions as well as a lower combined emitted C content. However, while WP biochar showed higher values for emitted C, it also contained substantially higher amounts of stored C. Therefore the feedstock choice could be determined by whether

C sequestration or heat/power generation is the preferable outcome during biochar production. At 650^{o}C the difference between feedstock was minimal but still visible, meaning feedstock selection could also be affected by the variation of other properties (CEC, nutrient availability, pH etc.) between different types of biochar.

Chapter 6 focused on the influence that production conditions had on the gas composition and energy content, while also assessing the possibility of sustaining a pyrolysis process using the gas stream alone. This possibility would free up the liquid and biochar co-products to be used for high value chemical synthesis and soil amendment respectively, without needing to sacrifice either of these valuable resources to power the pyrolysis process. To assess the potential for a self-sustaining pyrolysis process, the energy content of the pyrolysis gas, under different processing conditions, was compared against the lower (6 % biomass HHV) and the upper estimates (15 % biomass HHV) for the heat of pyrolysis. The results showed that pyrolysis at HTTs $\geq$ 450^{o}C consistently, for all production conditions, produced a gas product with a sufficient energy content to meet the lower energy limit (6 % biomass HHV), while the upper energy limit (15 % biomass HHV) was only reached for pyrolysis at 650^{o}C. However the upper energy limit of 15 % was obtained from a study using 'fast pyrolysis', and was substantially higher than other reported energy limits for the heat of pyrolysis (< 9 % biomass HHV). Surpassing these energy limits was possible for pyrolysis at $\geq$ 550^{o}C and so still deemed to be important for achieving a sustainable system. Sustaining the pyrolysis process based solely on the combustion of the gas stream would increase the utilisation of biochar and pyrolysis liquids for high-value products, but also diminish the energy input associated with fossil fuels, and hence reduce the C emissions of the overall biochar production process. While these results set important considerations for the future selection of pyrolysis conditions and what they could mean for the overall energy balance of the pyrolysis system, the energy limits used only represented the required heat of pyrolysis, and so did not account for heat transfer efficiency and the energy input needed to reach the different temperatures, since these are very much process/equipment dependent. Therefore detailed engineering studies followed by

LCA studies involving industrial biochar production processes would be needed before the implications of these results can be fully understood.

Therefore the combined results of Chapters 5 and 6 showed that pyrolysis at higher temperatures not only increased the energy contained within the liquid and gas fractions, and thus the potential energy output supply of the pyrolysis system, but also increased the C sequestration potential of biochar. Furthermore, the energy stored within the gas stream could provide adequate energy to sustain the pyrolysis process and partially dry feedstock, thus reducing the need of external energy sources such as fossil fuels.

The results of this thesis can start to provide the evidence needed to better understanding the trade-offs between the multiple benefits of biochar, and help to convert the qualitative assessments proposed by Jeffery *et al.* (2013) to quantitative values. However this is only an initial step which, used in conjunction with LCA, could aid in determining how each trade-off or benefit of biochar should be weighed (Jeffery *et al.*, 2013), and from this refine the pyrolysis system to attempt to maximise the environmental impact of biochar and recovery of energy from co-products.

8.3 **Bespoke biochar: A dream or reality**

The concept for biochar has been developed from observations made on the highly fertile terra preta soils; however it still remains to be seen whether these benefits can be matched following the addition of biochar to soil. Biochar research is overpopulated by hundreds of types of biochar produced from hundreds of types of feedstock under various production conditions. Therefore the heterogeneous nature of biochar, shown by large variation in chemical composition and structure, leads to a large uncertainty over its expected agronomical response, affecting any comprehensive agreement within the biochar community on suitable biochar properties. With few exceptions, research seems to have focused on simply producing biochar rather than truly investigating the production of the right type of biochar. There is a need for a complete and objective approach to biochar production

to aid in the economic success of the system (Spokas *et al.*, 2012) through optimizing the benefits of all co-products. Therefore for biochar to generate agronomical benefits, it is vital to understand how the quality of biochar is affected by the selection of feedstock and pyrolysis conditions (Antal & Grønli, 2003; Novak *et al.*, 2009).

Throughout this thesis several production conditions have been changed to explore their influence on important biochar properties as well as on the energy balance of the system. Production conditions can have varying degrees of influence on biochar properties, which make the process of maximising each property impossible. However, studying the variation of biochar properties with changing production conditions can aid in identifying regions where important modifications in biochar properties can occur, as well as detecting potential production conditions which have little or no influence on biochar properties. The findings of Chapters 3, 4, 5 and 6 can provide a better understanding of how the pyrolysis process can be engineered to minimise potential trade-off between key aspects of biochar while identifying production conditions under which biochar with improved environmental performance can be produced.

Refining the pyrolysis process to produce biochar with selectively engineered properties is only the start of achieving bespoke biochar. There are other factors which need to be considered to achieve a successful and effective product when applied to soil. In addition to pyrolysis conditions these factors include the reproducibility of biochar following the scale-up of pyrolysis, feedstock suitability (cost, availability, properties etc.); as well as accounting for local climate conditions, soil type and native soil biota (Czimczik & Masiello, 2007; Spokas *et al.*, 2012; Jeffery *et al.*, 2013). The variation between one location and the next for biochar application has resulted in positive performance of biochar in some cases, and negligible impact in other cases (Novak *et al.*, 2014). This makes optimisation of a biochar product extremely difficult and costly due to the need for site specific characteristics, rather than being able to mass produce a particular type of biochar. Increasing the scale of pyrolysis as well as identifying the variation between soil

properties are the next logical steps towards the development of bespoke biochar and are discussed further in the final section of this thesis.

Questions still arise over the positive and negative outcomes of field-scale application of biochar to the environment as well as the economic feasibility of biochar commercialization. In spite of these concerns, biochar application continues to show positive responses in various locations around the world. Jeffery *et al.* (2011) gave a general estimation of 10 % increase in crop productivity based on 16 studies; while the meta-analyses carried out by Biederman & Harpole (2013) (over 350 studies) and Liu *et al.* (2013) (103 studies) also showed that overall biochar addition resulted in increased aboveground productivity, increase crop yield, improved alkalinity of soil and a higher influence of alkaline biochar on soil pH. While Spokas *et al.* (2012) also reported that 50 % of published reports showed a short-term positive effect of biochar addition and 30 % showed no significant difference, 20 % actually reported negative yields. It is these unwanted negative effects of biochar which led to the concept of designer biochar, created to produce tailored properties for producing positive effects on selected soil constraints (Novak & Busscher, 2013).

The addition of biochar during these studies generally showed improvements or no harm to the ecosystem including plant productivity and soil nutrient content. Combine that with the evidence provided within this thesis for the effect of production conditions on the environmental and energy balance of biochar production, and biochar as a concept can become an attractive and realistic alternative solution for reducing atmospheric CO_2 and dependency on fossil fuels. At the very least, using soil as a C sink could help slow the rise of atmospheric CO_2 as societies search for alternative fuel sources to burning fossil C (Janzen, 2006).

The development of a niche market for specialized biochar could be the objective to substantially improve the economic picture for biochar production in particular where the production of ‘designer biochar’ for enhancing a specific soil deficiency is the desired end product (Novak & Busscher, 2013). However, separating the soil-

enhancing benefits of biochar from its C sequestration potential might be necessary to continue the development of biochar as a form of highly stable C which could be considered for C abatement markets (Spokas *et al.*, 2012). The potential end uses of biochar are virtually endless (Schmidt, 2012; Spokas *et al.*, 2012) and pyrolysis could be optimised to benefit these niche markets, of which not all are specific to soil application, although the argument would then be over the true definition of biochar.

8.4 Future challenges and conclusions

This study investigated a range of production conditions and the effect they have on the C sequestration (Chapter 3, 4 and 5) and soil enhancing potential (Chapter 4) of biochar as well as the potential energy output supply of pyrolysis (Chapter 5 and 6). These results have demonstrated that combinations of pyrolysis conditions exist under which it is possible not only to increase the potential energy output supply from pyrolysis but also to maintain the C mitigation potential of biochar and produce properties which could improve soil fertility. Therefore this work has set down considerable groundwork to refine the pyrolysis process for maximising a particular benefit of biochar or minimise the trade-offs between a combination of benefits. While both of these outcomes are vital to the realisation of bespoke biochar, this work has only completed the first step towards optimising the pyrolysis process. To realise the final goal of bespoke biochar deployment, two further areas of research are required. Firstly, exploring the true agronomic response of biochar and its ability to address key soil constraints under different environmental conditions (soil type, climate conditions etc.). Secondly, determining how increasing the scale of pyrolysis from small-scale to industrial-scale would influence the agronomic and economic feasibility of biochar production. Both of these topics are crucial to any potential for the production of a biochar product designed to improve a specific soil constraint in a selected location.

Although this thesis reports the results of laboratory screening tools to rapidly assess several biochar functional properties, there has been no consideration of the vast number of environmental variables (bulk density, soil composition, soil pH, climate

etc.) which would undoubtedly determine the final soil amendment potential of biochar. For example, biochar with high water retention and mechanically strength might be more valuable in an area with root crops on calcareous sandy arable soils and a dry climate than in an area of predominantly combinable crops on acidic sandy soils and a 'year round' wet climate (Verheijen *et al.*, 2009). Therefore well designed long-term field studies are crucial for exploring the mechanisms which lead to improved crop production across a wide range of agricultural conditions, the duration of these positive impacts as biochar ages, and regional differences that soil type and climate may have on biochar's environmental response (Jeffery *et al.*, 2011; Lehmann *et al.*, 2011; Gurwick *et al.*, 2013; Liu *et al.*, 2013). Biochar can currently be made from a seemingly limitless array of feedstocks and production conditions; therefore a standardised set of several biochar types should be produced under well-defined conditions to capture the most important differences in biochar properties adequately. Then by making these standards available to the research community, the reproducibility of comparable results between research methods as well as knowledge of soil and environmental factors can be gained and applied to improving the optimisation of biochar production. This is logically the next step towards the optimisation of the pyrolysis process towards the production of bespoke biochar. However such a task would be too great for one institute to achieve; therefore initiating knowledge transfer networks and global collaborations between research institutions would hugely expand the range of conditions being investigated, and eliminate the repetition of field studies, increasing the contribution of biochar towards the global effort of carbon sequestration and most importantly start to answer the large uncertainties surrounding industrial-scale application of biochar. However before bespoke biochar can be deployed on an industrial scale, further questions need to be addressed concerning the reproducibility of key biochar properties as pyrolysis scale is increased.

All biochar samples discussed within Chapters 3, 4 and 5 were produced using a small-scale batch pyrolysis unit. The scale and type of equipment used allowed for accurate variation in production conditions while producing acceptable sample yields

for the required analytical procedures. While pyrolysis on a small-scale allowed for the high level of control needed to investigate the impact of production conditions and to identify regions of major property changes, the same control may not be achievable when using industrial-scale pyrolysis. The same type of biochar can be produced, no matter the scale or type of pyrolysis, when the particles are exposed to the same thermal history and environment (within the reactor) as those applied during the small-scale batch experiments performed in this thesis. However, the challenge is to achieve this on different scales. Whilst establishing a better understanding of the influence that production conditions have on the chemical, physical and functional properties of biochar was pivotal to refining the pyrolysis process to improve the environmental performance of biochar, how these properties as well as the overall energy balance of the system vary between pyrolysis type and scale is another unanswered question, one which is essential to the commercialisation of biochar. The overall control of production conditions may be significantly affected as the pyrolysis scale and type are varied. This could affect the scale and rate of chemical processes occurring during pyrolysis, the efficiency of heat transfer between particles and the energy requirements of the system, potentially altering the quality and environmental performance of biochar as well as the economic feasibility of the system. Biochar production on an industrial-scale is essential to the progression and importance of biochar as a carbon sequestration technology as well as its impact on local and global communities. Biochar production and incorporation in soil involves the combination of physio-chemical and biological routes to reduce the levels of atmospheric GHG; however not enough is yet understood to deploy this process on a large scale (Hammond *et al.*, 2011). The conclusions of this thesis have indicated, under highly controlled conditions, which pyrolysis parameters are best suited to enhance different biochar properties and aspects of the pyrolysis system. Therefore this work can be used to guide testing of biochar production on different scales and by different technologies. This would then give a better understanding of the influence, if any, that the scale of production has on the agronomic and energy benefits of biochar as well as its feasibility as a marketable product.

While key production conditions (HTT, heating rate, residence time, carrier gas flow rate and feedstock) were extensively covered throughout this thesis, through > 100 pyrolysis experiments, there is an endless array of different parameters which can be varied during the pyrolysis process. Investigating a larger number of these parameters would have diminished the level of investigation possible and vice versa. If more time had been available then further studies on additional production conditions would have been considered, as well as additional functional properties to expand the systematic set of biochar samples and the size of data set for determining statistical relationships. One parameter considered prior to pyrolysis which was not investigated to a high enough degree was that of initial feedstock, but more specifically the component concentrations (i.e. cellulose, hemicellulose, lignin and ash) and particle size. The early stages of the PhD had initially planned for experiments to test how varying the concentration of individual biomass components such as lignin in the same feedstock type would affect the final biochar product. However sourcing of such material proved problematic. Therefore the feedstock used during the pyrolysis runs was analyzed to quantify the concentrations of cellulose, hemicellulose and lignin in the biomass which was used to statistically test relationships between the feedstock composition and biochar properties. Six types of biomass (PC, RH, SP, WP, WS and WSP) were selected to test the hypotheses set out in this thesis, and although this gave an indication into the differences between feedstock and thus the potential influence feedstock composition could have on the final value of co-products, it could not be used to determine the statistical influence of individual components, due to each feedstock type containing a unique combination of cellulose, hemicellulose and lignin. While this thesis has briefly touched upon the influence of biomass components on biochar properties, a more comprehensive study to identify which components can be modified in an attempt to increase desirable biochar properties, such as long term stability and biochar yield, would substantially improve the ranking of appropriate biomass for biochar production.

In addition to biomass composition, the physical properties of feedstock, such as particle size, were not extensively studied. The particle size of biomass can impact the thermo-chemical reactions occurring during pyrolysis, influencing the development of pore structure, release of volatiles as well as the final surface area of biochar samples (Antal & Grønli, 2003; Demirbas, 2004). Although the physical properties of biochar have been well covered within literature, their influence on biochar functional properties is under-researched. Modifying the pore structure of biochar could directly influence properties such as water holding capacity, nutrient retention and microbial activity, as well as carbon degradation. In addition to biochar properties, the pretreatment of biomass to alternative forms such as pellets can improve the energy efficiency of the material while also improving benefits associated with transport and storage of biomass. A combination of these benefits could lead to improved economic feasibility for the system, but detailed studies would need to be performed into the influence that physical structure may have on the energy output of the system and biochar's environmental performance, as well as the cost that varying the physical structure might have on the production system as a whole. Expanding the range and number of pyrolysis conditions being used to produce biochar can strengthen the accuracy of any statistical models developed from systematic sets to predict key properties of biochar, thereby negating the need to analyse 100s of samples where a strong model can predict the outcome.

The realisation of bespoke biochar may lead to the expansion of a niche market for biochar, but this would leave the full potential of biochar unrealised if restricted to the high end of the market. However the ability to control the pyrolysis process to produce bespoke biochar can be valuable for lower value products as well. The production of a cheap and affordable biochar product will significantly improve the worldwide implementation of biochar and through this the C abatement potential of biochar; however such a product would depend on the technology and local sourcing of materials, especially in developing countries. The economic and practical feasibility of the pyrolysis-biochar system is largely dependent on cost of feedstock and the pyrolysis process (Roberts *et al.*, 2010; Shackley *et al.*, 2011). The

continuation of biochar's application as a soil amendment material will also depend on the strength of C markets, with the price of C crucial to the cost-effectiveness of biochar projects (Pratt & Moran, 2010; Roberts *et al.*, 2010). Given the low price for sequestered C incentives and relatively high cost of biochar production, the income received from the agronomic benefits of biochar must be higher than the biochar cost to maintain the economic feasibility of the process (Sohi, 2012; Liu *et al.*, 2013).

This thesis has systematically explored many important aspects of biochar production and how this process may influence key functional properties connected to the agronomic performance of biochar. This work has demonstrated significant findings to aid in refining the pyrolysis process to improve the C sequestration and soil enhancing potential of biochar, while highlighting the areas of future research needed to achieve deployment of bespoke biochar. This thesis has indicated that the potential exists for pyrolysis to be used for heat/power generation while at the same time provide long term C storage. This thesis has also emphasised that under certain conditions it is possible to produce biochar which demonstrates properties related to soil enhancing benefits, C sequestration and effective energy output through pyrolysis co-products. The outcomes of this thesis have therefore shown that the concept and potential of bespoke biochar does exist.

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Appendix 1. **Supplementary material**

Throughout the main body of this thesis, biochar samples were analysed using proximate and ultimate analysis. While the results of these tests provided useful composition data on biochar samples they were not always directly relevant to the aims of the chapter and therefore the interpretation of the results was minimised. However additional discussion of these results was collected and presented in the following section.

A1.1 **Chapter 3**

A1.1.1 **Carbon Yield results**

As HTT is increased the concentration of C in biochar also increases. However, this is not the case when the amount of C as a proportion of the initial feedstock C is taken into account. By representing the total C on a feedstock C basis the yield of C decreases over the temperature range 350°C – 650°C as shown in Figure A1-1.

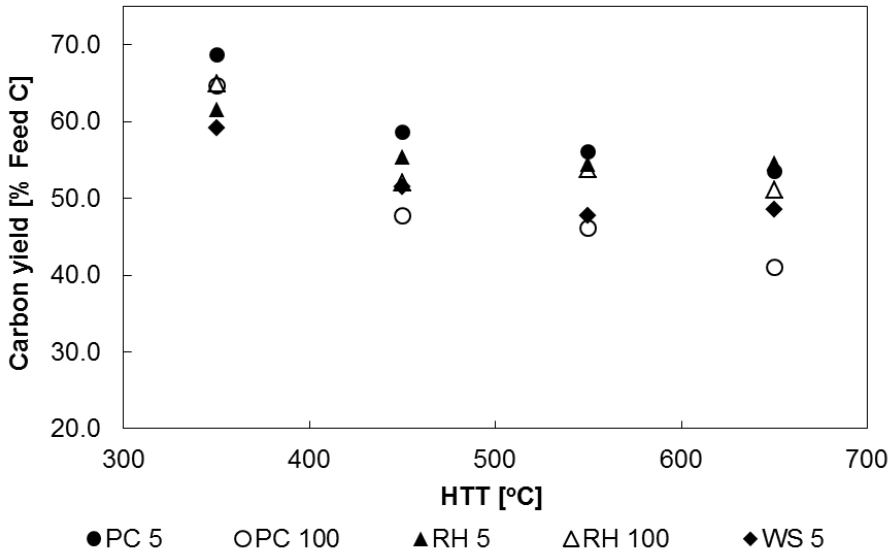

Figure A1-1: Variation of C yield with increasing production temperature. This figure has been amended from the published version to express C yield on a feedstock C % rather than feedstock wt. % basis. Error bars were added to the graph to show standard error of C % analysis but are not visible due to the scale of the data (n=2).

All biochar samples presented in Figure A1-2 had a lower H:C and O:C ratio than their parent biomass owing to preferential elimination of O and H relative to C in volatile matter. Both ratios decreased in biochar with increasing pyrolysis HTT. Decreasing values of H:C and O:C indicated increased biochar stability.

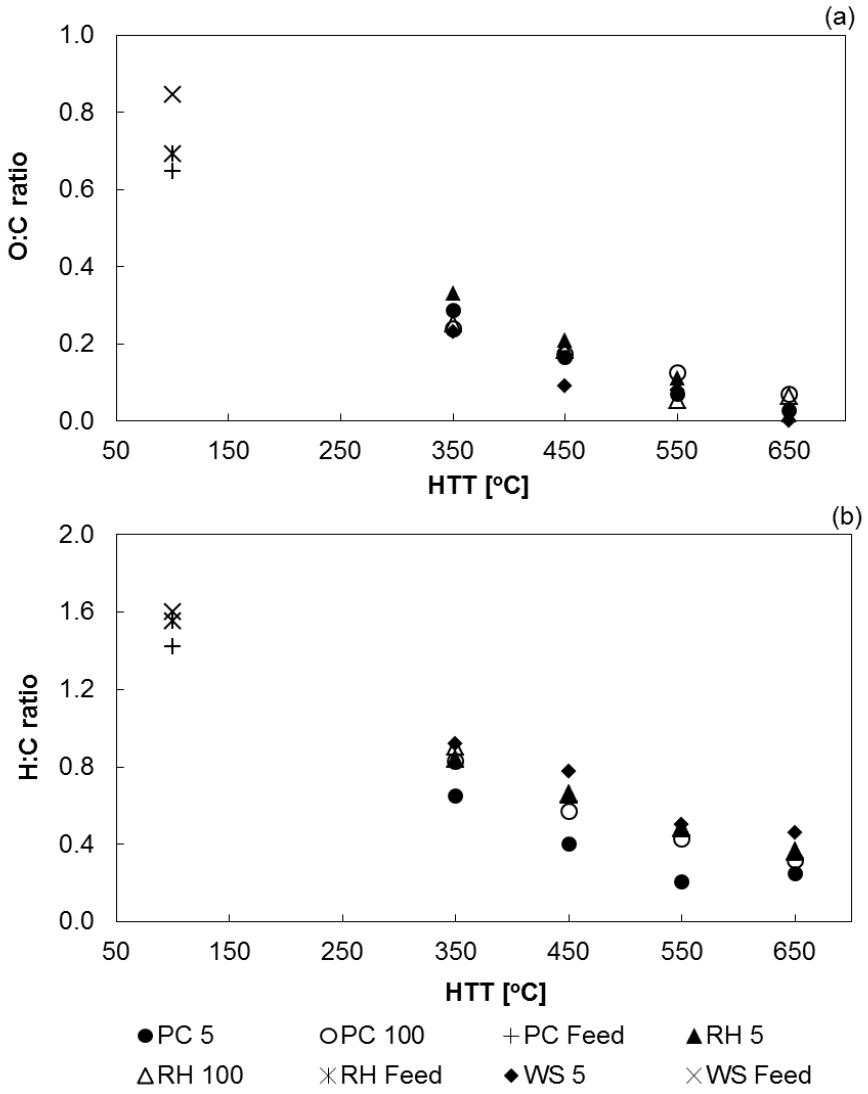

Figure A1-2: Influence of temperature on the (a) O:C ratio and (b) H:C ratio of biochar samples and parent biomass.

A1.1.2 Correlation between Proximate and Elemental analysis

The results obtained from proximate analysis were compared to those produced by elemental analysis to investigate the correlation between two different methods for stability determination. The correlation between techniques and accompanying R values are shown in Figure A1-3.

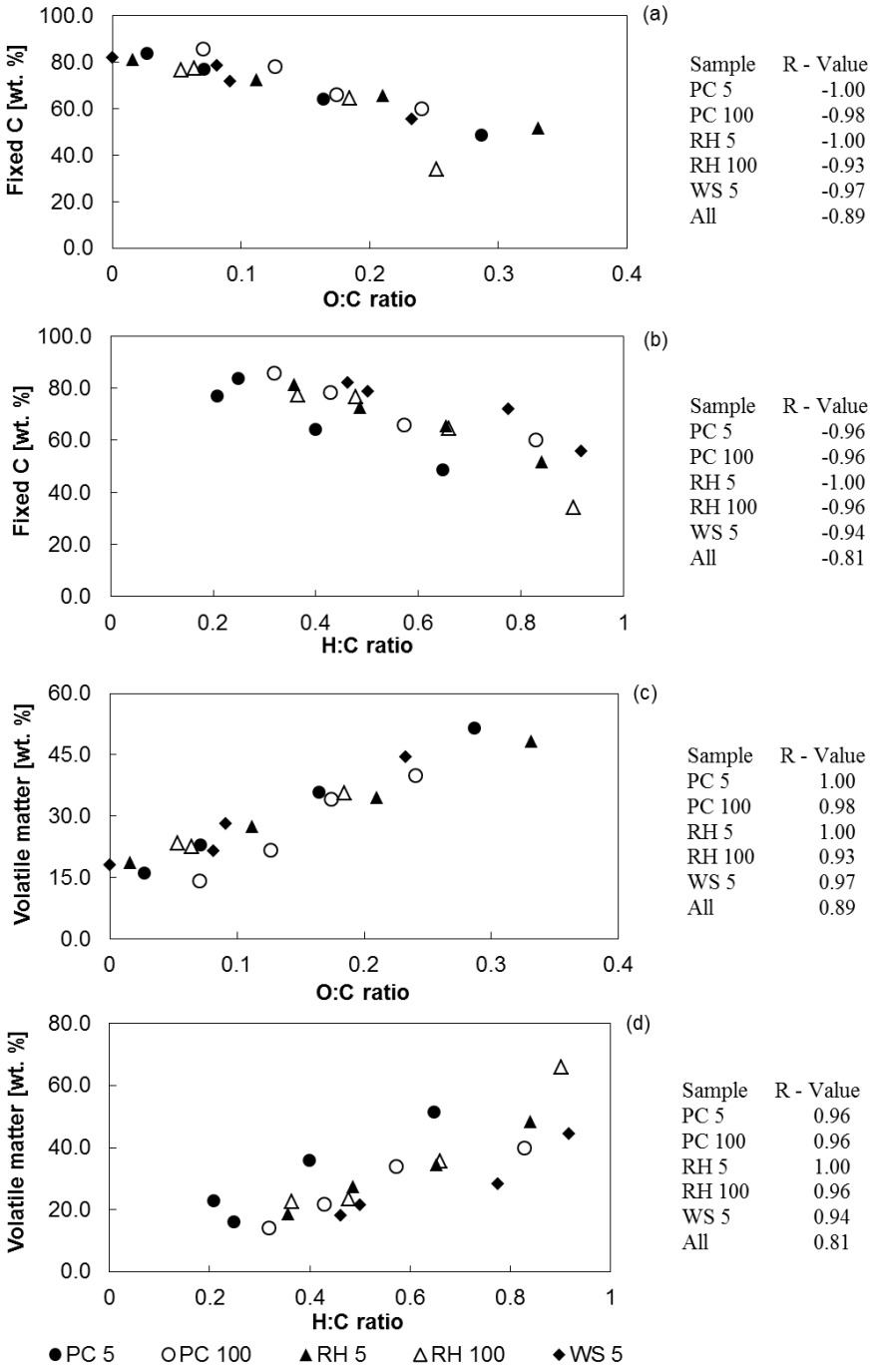

Figure A1-3: Comparisons between proximate and elemental analysis data to show correlations between (a) fixed C % vs O:C ratio (b) fixed C % vs H:C ratio (c) volatile matter % vs O:C (d) volatile matter % vs H:C ratio.

A1.2 **Chapter 4**

A1.2.1 **Product distribution**

Production yields for char, liquid and gas co-products obtained from each pyrolysis experiment are shown in Table A1-1. For each feedstock type, increasing the HTT caused the biochar yield to decrease and subsequently increase the liquid and gas yields. This is due to greater primary decomposition of biomass at elevated temperatures and the favorable production of non-condensable gases through secondary decomposition of char residue (Mohan *et al.*, 2006; Bruun *et al.*, 2011; Demiral & Ayan, 2011; Fu *et al.*, 2011; Enders *et al.*, 2012; Crombie *et al.*, 2013). When analyzing the full data set, HTT was seen to be the dominant variable in determining the distribution of the char, liquid and gas co-products ($P < 0.0001$) while feedstock only influenced the yield of gas produced during pyrolysis. PC biochar demonstrated the highest char yields while also showing the largest decline in char yield of ~ 19 % compared to WS (~ 11 %) and WSP (~ 14 %) biochar as HTT was increased from 350^{o}C to 650^{o}C. The liquid yields obtained from PC pyrolysis continued to increase with rising HTT while WS and WSP liquid yields appeared to reach a plateau around 550^{o}C , as observed in other studies (González *et al.*, 2003; Becidan *et al.*, 2007; Demiral & Ayan, 2011; Duman *et al.*, 2011). This maximum is a result of secondary cracking of vapours and char at higher HTT leading to producing increased gas yields and a reduction in bio-oil yield (González *et al.*, 2003; Demiral & Ayan, 2011).

Table A1-1: Product distribution, proximate and ultimate analysis of all biochar samples on dry weight basis (db) and dry ash free basis (daf).

	Product Distribution [wt.% (db)]			Proximate analysis [wt.% (db)]					Ultimate analysis [wt.% (db)]				
Sample	Biochar	Liquid	Gas	Fixed C	Volatile Matter	Ash	FC Yield (daf)	VM Yield (daf)	C	H	N	O	C Yield
PC350/5	49.2	31.7	19.1	47.8	50.8	1.4	33.3	35.4	70.8	3.9	0.0	24.0	68.7
PC450/5	36.8	39.1	24.1	62.2	34.9	2.9	37.6	21.0	80.8	2.7	0.0	13.6	58.6
PC550/5	32.0	42.5	25.5	73.9	22.0	4.2	43.2	12.8	88.8	1.6	0.0	5.5	56.0
PC650/5	28.1	48.7	23.2	78.9	15.2	5.9	44.8	8.7	90.9	1.9	0.0	1.3	53.5
PC350/100	41.4	45.3	13.3	58.0	38.7	3.4	38.8	25.8	70.1	4.9	1.4	20.4	64.6
PC450/100	29.1	51.4	19.5	63.6	33.0	3.4	31.5	16.3	77.2	3.7	1.0	14.6	47.8
PC550/100	25.4	53.6	21.0	77.7	21.6	0.7	36.1	10.0	85.9	3.1	0.9	9.5	46.1
PC650/100	23.0	54.8	22.2	81.6	13.4	5.0	35.2	5.8	84.7	2.3	1.4	6.6	41.0
WS350/5	39.0	40.0	21.0	49.5	39.6	10.9	32.8	26.3	65.2	5.0	1.6	17.3	59.1
WS450/5	31.2	41.3	27.5	59.2	23.2	17.6	36.9	14.5	71.0	4.6	1.2	5.7	51.4
WS550/5	29.0	38.8	32.2	62.8	17.2	20.0	37.5	10.2	70.8	3.0	0.7	5.5	47.7
WS650/5	27.3	35.0	37.7	64.4	14.2	21.3	39.8	8.8	76.6	3.0	1.2	0.0	48.6
WS350/100	41.2	40.9	17.9	50.3	34.6	15.2	36.0	24.7	63.5	3.1	1.6	16.6	60.7
WS450/100	34.7	41.9	23.4	57.9	22.6	19.6	37.1	14.5	64.0	2.4	1.3	12.6	51.6
WS550/100	29.8	45.0	25.2	62.9	17.4	19.7	37.7	10.5	69.6	1.6	1.4	7.7	48.2
WS650/100	29.4	42.7	27.9	55.5	16.9	27.6	32.4	9.8	61.9	0.9	1.3	8.3	42.2
WSP350/5	43.7	35.4	20.9	46.0	39.6	14.4	31.0	26.8	63.4	4.3	1.4	16.5	57.8
WSP450/5	35.0	41.5	23.5	55.6	26.8	17.6	32.8	15.8	66.7	3.2	1.7	10.8	48.6
WSP550/5	31.7	45.7	22.6	62.7	17.2	20.1	36.3	9.9	70.0	2.4	1.3	6.2	46.2
WSP650/5	29.7	43.0	27.3	64.8	13.3	21.9	36.0	7.4	70.3	1.6	1.1	5.1	43.4
WSP350/100	-	-	-	-	-	-	-	-	-	-	-	-	-
WSP450/100	30.5	42.5	27.0	59.2	19.9	20.9	31.4	10.6	66.1	2.7	1.2	9.1	42.0
WSP550/100	30.6	41.3	28.1	61.2	16.9	21.9	33.6	9.2	67.2	2.3	1.1	7.4	42.8
WSP650/100	27.8	40.1	32.1	65.1	11.1	23.7	32.6	5.6	65.9	1.0	1.1	8.3	38.2

Within the range investigated, heating rate showed no statistically significant influence ($P > 0.05$) on the final yields of char, liquid or gas over the entire data set. However when focusing on the effect of heating rate on each individual feedstock, the heating rate became important. Pyrolysis of PC and WSP at a heating rate of $100^{o}C\ min^{-1}$ clearly produced a lower yield ($P < 0.05$) of biochar compared to $5^{o}C\ min^{-1}$ while the pyrolysis of WS biomass at $100^{o}C\ min^{-1}$ produced higher char yields at each temperature. This influence on char yield was more prominent at lower HTT and the effect did diminish with increasing temperature similar to trends seen by Angin (2013). When focusing on individual feedstock, PC and WS exhibited increased liquid yields when applying the higher heating rate while WSP liquid yields were very similar to those obtained when using $5^{o}C\ min^{-1}$ indicating that the maximum liquid yield had been achieved at both heating rates. At higher heating rates the pyrolysis reactions occur over a shorter period of time and therefore increased concentration of volatile material is emitted resulting in increased liquid yields (Angin, 2013). By analyzing the gas yield data separately for PC, WS and WSP experiments the importance of feedstock becomes apparent. At the $5^{o}C\ min^{-1}$ biomass is slowly heated and pyrolysis progresses through well-described stages of biomass decomposition (Raveendran, 1996; Yang *et al.*, 2006a) allowing for sufficient time for volatiles to diffuse from within the particles promoting the formation of char and liquid fractions (Becidan *et al.*, 2007; Angin, 2013). When the heating rate is elevated to $100^{o}C\ min^{-1}$ the release of volatiles becomes rapid and feedstock components all undergo decomposition almost simultaneously (Williams & Besler, 1996; Becidan *et al.*, 2007; Isahak *et al.*, 2012) causing an accumulation of volatiles between and within particles (Angin, 2013). This leads to substantially increased interactions between the char, liquid and gas fractions minimising the differences seen in char yields between different feedstock. Several studies found that cracking reactions occurring above $500^{o}C$ at high heating rates ($100^{o}C\ min^{-1}$ – $500^{o}C\ min^{-1}$) favoured the formation of gas products rather than that of liquids leading to decreasing liquid yields above $600^{o}C$ (Williams & Besler, 1996; Tsai *et al.*, 2006; Demiral & Ayan, 2011; Isahak *et al.*, 2012). This observation could

explain why liquid yields obtained using 100^{o}C min^{-1} for pyrolysis of PC and WSP at 650^{o}C were lower than those produced using 5^{o}C min^{-1}.

A1.2.2 **Proximate analysis**

Results for proximate and ultimate analysis on all biochar samples are also shown in Table A1-1. For the majority of samples ash concentration was seen to increase with increasing HTT as well as show variation between different feedstock types. Feedstock ($P < 0.0001$) and HTT ($P < 0.001$) were both deemed to show significant influence on the ash concentration of biochar while heating rate had no impact ($P > 0.05$). Biochar derived from straw material showed substantially higher ash content of 27.6 % and 23.7 % for WS and WSP respectively compared to 5 % for PC at the same HTT. While the heating rate had no overall significant influence on ash content, for the majority of samples the higher heating rate of 100^{o}C min^{-1} produced a higher ash content compared to 5^{o}C min^{-1}. Biochar fixed-C and volatile matter concentrations on a dry basis were both found to be affected ($P < 0.05$) by feedstock and HTT however this could be down to the influence of ash content on both of these properties. When represented on a dry ash-free basis fixed-C and volatile matter are still greatly dependent on HTT ($P < 0.0001$) however feedstock no longer has a statistical impact ($P = 0.54$). The fixed-C content of biochar increased with HTT due to higher emissions of volatile compounds at elevated temperatures. At 650^{o}C the volatile matter concentrations of all biochar samples were relatively similar (11.2 – 16.6 %). However at low HTT (350^{o}C) the difference between wood and straw based biochar is clear with PC biochar generally containing the highest concentration of volatile matter as well as the largest decrease of 50.8 % to 15.2 % as HTT was increased from 350^{o}C to 650^{o}C (5^{o}C min^{-1}). PC biochar also achieved higher fixed-C content of > 77.8 % at 650^{o}C compared to < 64.4 % and < 65.1 % for WS and WSP biochar respectively. Heating rate showed no statistical influence on the concentrations of fixed-C or volatile matter.

As HTT is increased the biochar yield decreases meaning that although there is higher fixed-C content at elevated temperatures the amount of biochar diminishes. This is why it is important to represent fixed-C and volatile matter on a feedstock C

basis to produce fixed-C and volatile matter yields (Table A1-1). This allows for the determination of what proportion of original feedstock C is retained as fixed-C and volatile matter within the final biochar samples. The volatile matter yield followed the same trend as volatile matter content by decreasing with increasing HTT although over a smaller scale. The fixed-C yield of biochar was seen to be unaffected by the selected HTT meaning that enhancing the intensity of pyrolysis would not reduce the amount of feedstock C in the form of fixed-C. This observation has also been confirmed through additional studies (Antal & Grønli, 2003; Crombie *et al.*, 2013; Mašek *et al.*, 2013a).

A1.2.3 **Ultimate analysis**

The C content of biochar increased with pyrolysis HTT (and inversely to biochar yield) through the preferential elimination of N, H and O as volatile matter (Baldock & Smernik, 2002; Antal & Grønli, 2003; Novak *et al.*, 2009; Bruun *et al.*, 2011; Crombie *et al.*, 2013). The elimination of O and H is a result of the scission of weak alky-aryl ether bonds during the formation of more resistant structures (Baldock & Smernik, 2002; Demirbas, 2004; Novak *et al.*, 2009). Statistical analysis indicated that feedstock, HTT and heating rate were determining factors on CHNO concentrations but each variable affected different elemental concentrations.

Feedstock, HTT and heating rate were all seen to influence ($P < 0.05$) final concentration of C present in biochar samples. The total C content PC biochar increased from 70 % to > 85 % for both heating rates as HTT was increased from 350^{o}C to 650^{o}C. As with fixed C, the PC demonstrated a substantially larger increase in total C than both WS (65 – 76 %) and WSP (63 – 70 %) material. The higher C content of high HTT biochar could be a direct result of the lower ash concentration of pine compared to wheat (Novak *et al.*, 2009; Enders *et al.*, 2012). When a higher heating rate was applied the total C concentration remaining within biochar was consistently lower than that obtained using 5^{o}C min^{-1}. HTT was also deemed to have a statistical influence on the concentrations of H and O and therefore also affect the O:C and H:C biochar ratios. These ratios have been previously used (Crombie et al., 2013 (Chapter 3); Crombie & Mašek, 2013 (Chapter 5); Hammes et al., 2007; IBI,

2013; Preston & Schmidt, 2006; Schmidt et al., 2012; Spokas, 2010) to indicate the degree of carbonization during pyrolysis and assessment of long term stability. The diminishing H and O content with HTT lead to lower O:C and H:C ratios at higher pyrolysis HTT indicating a higher degree of biomass conversion and therefore increased biochar stability. At HTT > 450^{o}C all biochar samples had a O:C ratio lower than 0.2 which according to Spokas (2010) relates to biochar stability of >1000 years. The C yield was also calculated by determining the proportion of initial feedstock C remaining within each biochar sample. This demonstrated that although the biochar C content increased with rising HTT the overall yield of C actually diminishes at higher temperatures due to a lower amount of biochar produced at elevated pyrolysis HTT.

Appendix 2. **Comparison of microwave and conventional pyrolysis for biochar production**

During the PhD additional project work was carried out with the University of York studying the comparison between conventional (slow) pyrolysis (CP) and microwave pyrolysis (MW), and resulted in two journal publications. However, as these projects involved multiple contributors whether during sample production, sample analysis or the publication of results, it did not warrant separate chapters within the main body of the thesis. The following section will outline the methodology and results behind the collaboration with the University of York.

A2.1 **Project outline**

Pyrolysis runs were performed to compare the effect of using MW or CP for biochar production. The use of CP has been extensively studied throughout the main chapters of this thesis however it was important to continue to expand the data collected about the influence of process conditions when using different types of pyrolysis. Therefore the aim of the work was to investigate the differences that applying MW and CP pyrolysis has on the properties of biochar as well as the energy balance of the system. The production of biochar via MW was carried out by the University of York while the CP experiments were completed at the UKBRC.

A2.1.1 **My contribution**

The first step of the project work involved the production of two systematic sets of biochar samples, with one set produced using MW and the other by CP. Following sample production, the next step in the project was the analysis of biochar for physicochemical properties such as elemental composition, heating value and porosity as well as the functional property of C stability. During the project the candidate was solely responsible for the production of biochar samples using CP, analytical analysis of MW and CP biochar samples for C stability (as described in section 2.4.2.1.1), writing of related sections in the following publications as well as reviewing the overall manuscripts before submission.

A2.2 **Materials**

The two types of biomass used in all experiments were as follows: willow wood chips (6mm, WC), supplied by Renewable Energy Suppliers Ltd. (Retford, Nottinghamshire, England, Koolfuel 15), and mixed 50/50 wheat:oilseed rape straw pellets (6mm, SP) from Straw Pellets Ltd. (Rookery Farm, Lincolnshire, England). Feedstock was used as received with no additional pre-processing and moisture content measured (gravimetrically loss on drying at 105^{o}C for 24 hr.) at 10.8 % and 5.4 % for WC and SP respectively. Biomass feedstock composition was presented in Table A2-1.

Table A2-1: Biomass feedstock composition. Elemental data represented on dry weight basis (db) while biomass components presented as received (ar).

Feedstock	C [%(db)]	H [%(db)]	N [%(db)]	Ash [%(ar)]	Moisture [%(ar)]	Cellulose [%(ar)]	Hemicellulose [%(ar)]	Lignin [%(ar)]
Willow chips (WC)	48.3	6.0	1.0	0.8	9.1	37.2	36.0	18.7
Straw pellets (SP)	45.3	6.0	0.4	3.9	6.7	28.2	44.2	17.0

A2.3 **Pyrolysis**

Pyrolysis of slow pyrolysis biochar samples was performed at the UKBRC while MW was used at the University of York to produce the second systematic set of biochar.

A2.3.1 **Conventional pyrolysis**

Initial set up of equipment and procedure for collection of solid, liquid and gas fractions was performed as described in section 2.3. The feedstock sample (approximately 60 g for WC and 100 g for SP) was heated at an average rate of 5^{o}C min^{-1} to the required higher heating temperatures of 200^{o}C, 250^{o}C, 300^{o}C and 350^{o}C. The peak pyrolysis temperature was maintained for 10 minutes before the heating was stopped and the sample cooled under nitrogen.

A2.3.2 **Microwave pyrolysis**

A full description of the experimental set up for MW can be found in Mašek *et al.* (2013) and Gronnow *et al.* (2013). Briefly, MW was carried out using a Milestone ROTO SYNTH Rotative Solid Phase Microwave Reactor (Milestone Srl., Italy) fitted in series with a VAC 2000 vacuum module (Figure A2-1). A maximum power of 1200 W with an operating microwave frequency of 2.45 GHz was used to treat the biomass sample. Biomass (ca. 130 g WC, ca. 175 g SP) was placed in a 2 L glass flask within the microwave cavity and MW was carried out under constant microwave power (1200 W) and vacuum.

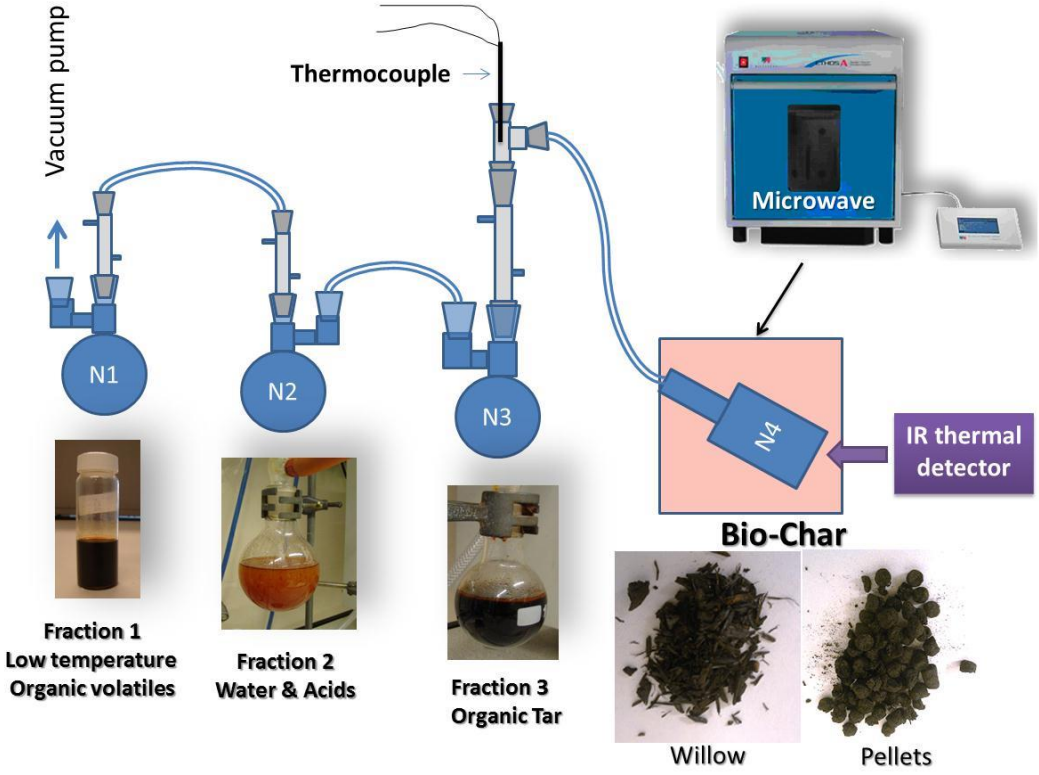

Figure A2-1: Microwave pyrolysis setup at The University of York.

A2.4 **Results**

The following section details the results of the analytical work carried out on biochar produced by CP at UKBRC. The focus of this work was to compare the product yields obtained from CP and MW with particular interest in the recovery yields and properties of the solid fraction (biochar). Although MW biochar was not produced as part of the PhD project the analytical results were still included in the below results to demonstrate the contrast between the two methods of pyrolysis. UKBRC results were then combined with analytical and interpretation work carried out by colleagues at the University of York and the overall collaboration was presented in Mašek *et al.* (2013) and Gronnow *et al.* (2013).

A2.4.1 **Product distribution**

The yields obtained for solid, liquid and gas co-products from CP and MW are shown in Table A2-2. Initially there is a clear difference in the distribution of products between the two types of pyrolysis. For CP at 200^{o}C there was little to no conversion of biomass shown by very high solid yield of 98.1 % and 93.9 % for WC and SP respectively. MW at a similar temperature lead to much higher liquid (> 28.7 %) and gas (> 30.5 %) yields as well as the resulting lower char yield (< 33.7 %) demonstrating a considerably higher degree of breakdown compared to CP. Even though CP at 350^{o}C resulted in improved biomass decomposition it was still not as efficient as MW. This effect has been attributed to the activation of amorphous cellulose under microwave irradiation (Gronnow *et al.*, 2013).

Table A2-2: Pyrolysis product yields.

Sample		Temperature [°C]	Char [wt.% (db)]	Liquid [wt.% (db)]	Gas [wt.% (db)]
Straw pellets	SP MW	200	33.7	28.7	37.6
	SP 200	200	93.9	4.8	2.6
	SP 250	250	66.3	20.2	16.5
	SP 300	300	46.6	32.9	23.9
	SP 350	350	49.9	31.6	21.6
Willow chips	WC MW	170	27.3	42.2	30.5
	WC 200	200	98.1	1.2	0.7
	WC 250	250	83.2	9.7	4.8
	WC 300	300	53.2	30.1	14.7
	WC 350	350	39.8	39.9	20.2

A2.4.2 **Stable-C**

The highly recalcitrant nature of biochar is arguably the main reason for the increased global research into pyrolysis and biochar production, making the assessment of this stable fraction vital to the progression of biochar as a marketable product. The influence of temperature on the concentration of total C and stable-C as well as overall stable-C yield were shown in Table A2-3.

Table A2-3: Char yield, carbon content, stability and stable carbon yield of biochar produced from MW and CP.

Sample		Temperature [°C]	Char % [wt.% (db)]	C % [wt. % (db)]	C Yield [wt.% C-basis]	C Stability [wt.% Char-C]	Stable C Yield [wt.% C-basis]
Straw pellets	SP MW	200	33.7	57.8	43.0	57.6	24.8
	SP 200	200	93.9	48.1	99.7	46.5	46.3
	SP 250	250	66.3	53.0	77.5	n.a.	n.a.
	SP 300	300	46.6	57.1	58.4	53.7	31.3
	SP 350	350	49.9	57.0	62.7	48.6	30.5
Willow chips	WC MW	170	27.3	65.2	36.9	58.0	21.4
	WC 200	200	98.1	49.1	99.7	44.8	44.7
	WC 250	250	83.2	53.7	92.5	42.6	39.4
	WC 300	300	53.2	69.5	76.6	45.0	34.5
	WC 350	350	39.8	70.7	58.2	60.5	35.3

Increasing the pyrolysis temperature increases the breakdown of the biomass material promoting the release of H and O causing the total C content to also increase

with temperature. By taking the decreasing char yield into account the C yield (feedstock C basis) can be seen to also decrease as the pyrolysis temperature during CP is increased. For both biomass materials the C yield is near 100 % at 200^{o}C but falls to 62.7 % and 58 % at 350^{o}C for SP and WC biochar respectively. Biochar produced by MW showed comparable C content with CP at 350^{o}C although the temperature of MW was approximately 150^{o}C lower. The smaller char yield obtained for MW also attributed to a lower C yield for MW biochar compared to CP biochar at all temperatures. The overall trend of C stability is more complicated than that of C and char yields. There is little variation in the C stability for CP biochar produced below 350^{o}C potentially due to the small degree of biomass breakdown below this temperature. For CP the highest C stability measures were obtained from SP produced at 300^{o}C and 350^{o}C for WC which was comparable to the C stability concentration of MW biochar. The stable-C yield was seen to decrease slightly with increasing CP temperature with the lowest values of 30.5 % and 34.5 % seen for SP at 350^{o}C and WC at 300^{o}C respectively. While MW biochar showed relatively high stability the low char yield also associated with MW resulted in very low stable-C yields for both materials (21 – 25 %). Therefore although MW operated at a lower production temperature (170^{o}C – 200^{o}C) and produced high stability biochar the overall C sequestration potential of the technology is limited by a low stable-C yield.

A2.5 **Results of collaboration**

The following section briefly summarises the main conclusions from the collaboration work, presented in detail in Mašek *et al.* (2013); Gronnow *et al.* (2013).

A2.5.1 **Microwave and slow pyrolysis biochar – Comparison of physical and functional properties** (Mašek *et al.*, 2013b)

The focus of this publication was to compare the physical and functional properties of biochar produced from MW and CP pyrolysis to evaluate how the type of pyrolysis might affect the properties of biochar.

When CP was carried out at temperatures < 300^{o}C minimal transformations occurred indicating some signs of hemicellulose breakdown. This was not the case when MW was used for biomass conversion. The different method of heating involved in MW resulted in considerable transformation of biomass releasing more volatiles from SP at 200^{o}C than at 350^{o}C for CP. The higher degree of conversion seen during MW was also reflected in the C stability of the biochar. Biochar produced by MW at 200^{o}C (SP) and 170^{o}C (WC) demonstrated comparable or increased stability than biochar obtained by CP at 300^{o}C – 350^{o}C. Although the stable-C concentration was similar or higher for MW the C yield obtained was considerably lower. Therefore a lower stable-C yield was obtained for MW compared to CP resulting in a lower carbon sequestration potential for the temperature range investigated. Although MW would appear to be less efficient at storing C in the form of biochar its higher potential for generating renewable energy co-products could turn out more beneficial (section A2.5.2). However detailed LCA would need to be carried out as well as expanding the production conditions and biochar properties investigated.

A2.5.2 **Torrefaction/biochar production by microwave and conventional slow pyrolysis – comparison of energy properties** (Gronnow *et al.*, 2013)

Although the samples used within this publication were the same as those presented in Mašek *et al.* (2013) the focus of this manuscript was to assess the energy balance of MW compared to CP.

A2.5.2.1 **Calculated energy input required for solid fuel production**

The required electrical energy for MW of wood chips was estimated at approximately 1080 MJ t^{-1}. However when the average efficiency (38 %) of converting heat energy to electrical power is considered the overall energy requirement to convert wood to stable carbon via MW becomes 3000 MJ t^{-1} (3.0 kJ g^{-1}). When applying CP rather than MW the energy required to pyrolysis 1 ton of WC was calculated at 1173 MJ t^{-1}. Although the energy required for CP was higher than that for MW, conventional heating does not necessarily require a conversion from heat energy to electricity. The energy required for CP can be calculated as 6 % of the HHV of the original feedstock compared to 17 % feedstock HHV for total MW energy. The energy requirements are also shown to be lower for CP when a required mass of biochar is needed. Due to the higher char yield obtained from CP the energy required to produce 1 ton of biochar was calculated as 2940 MJ t^{-1} which is approximately one-third the required energy of MW (11720 MJ t^{-1}).

Combining the two different methods of heating could have added benefits. By applying conventional heating as part of a pre-treatment step to near pyrolysis temperatures (160 – 180^{o}C) then the high energy input and heating rates associated with MW can be used for the final biomass conversion step. This could substantially reduce the processing time and operating temperature while maintaining an energy advantage over a CP approach.

A2.5.2.2 **Energy of solid and volatile fractions**

The majority of emitted volatiles during pyrolysis are easily combustible and therefore a good source of stored energy which can be extracted through direct

combustion within a CP system or other technologies such as established internal/external combustion engine. The recovery and installation of any such technology brings additional costs to the system but would be beneficial to the economics and practicality of the pyrolysis process.

CP was seen to be the more efficient process when sequestrating C was the desired outcome of the two technologies. However, when the difference in recovered energy from co-products is introduced to the fold overall MW could be the more attractive process. For MW a trade-off between the product energy content, energy released and required input energy is reached at 170^{o}C while for CP no energy has been released by 200^{o}C. The ideal situation would be to maximise the stable-C fraction within biochar while also optimising the agricultural benefits of biochar while needing minimal input energy. Both pyrolysis processes have relatively low energy requirements compared to the potential output energy from bio-oil and gas. CP used approximately half the energy required by MW however the output energy from MW was almost double that obtained from CP. Therefore pyrolysis by either technology would have high potential to be self-sufficient based on input requirements and the significant excess energy available from co-products. The determining factor would need to be the influence both technologies have on the environmental impact of biochar, a topic needing further research.

Appendix 3. **Direct oxidation of Cornell biochar samples**

During the PhD additional project work was carried out as part of collaboration with Cornell University. The following section will describe the work undertaken during a two month project (October to December 2012) within the Johannes Lehmann research group at Cornell University, Ithaca, NY. During my confirmation panel meeting it was suggested that I would benefit from a short stay at a foreign biochar research institute. After considering the potential options I made contact with Professor Lehmann at Cornell University and proposed a project where I could analyse the large biochar collection they had assembled. Funding for the project was achieved as a result of my successful application to the John Moyes Lessells travel grant organised through the Royal Society of Edinburgh. The funding was for the sum of £2500 which covered travel, accommodation, US visa and laboratory materials needed throughout my stay.

A3.1 **Project outline**

The aim of the project was to assess the environmental stability of biochar, produced and collected by those at Cornell University, using the direct oxidation tool developed at the UKBRC. This would then aid in expanding the data set of samples analysed using the direct oxidation tool without the time consuming process of biochar production.

A3.2 Materials and Methodology

Cornell biochar samples were produced at Cornell as well as external companies, under a range of production conditions and analysed for several biochar properties (Rajkovich *et al.*, 2011; Enders *et al.*, 2012). All samples were produced at temperatures between 250 – 600^{o}C from Pine (Pine), Hazelnut (HN), Corn Stalks (CS), Oak (Oak), Paper Waste (PW), Poultry Manure (PM), Bull Manure (BM), Dairy Manure (DM), Digested Dairy (DD) and Chinese bamboo (CB).

A3.2.1 Edinburgh stability tool

The Edinburgh stability tool was developed to rapidly screen biochar samples for long term stability by mimicking the environmental breakdown of biochar. The analytical procedure for the Edinburgh stability tool is described in section 2.4.2.1.1.

A3.3 **Results and discussion**

A3.3.1 **Biochar yield**

Biochar was produced using a wide variety of pyrolysis equipment under an array of production conditions. The gathering of this large biochar collection was for the characterization of key biochar properties presented in Rajkovich *et al.* (2011) and Enders *et al.* (2012). The yield of biochar is important when considering the overall mass yield of stable-C within a biochar sample. Therefore Figure A3-1 shows the degree of influence that temperature has on the biochar yield of the samples chosen for direct oxidation analysis. The char yield data was not available for all samples analysed for stable-C (i.e. CB) due to the acquisition of biochar from external sources and so were not included in Figure A3-1.

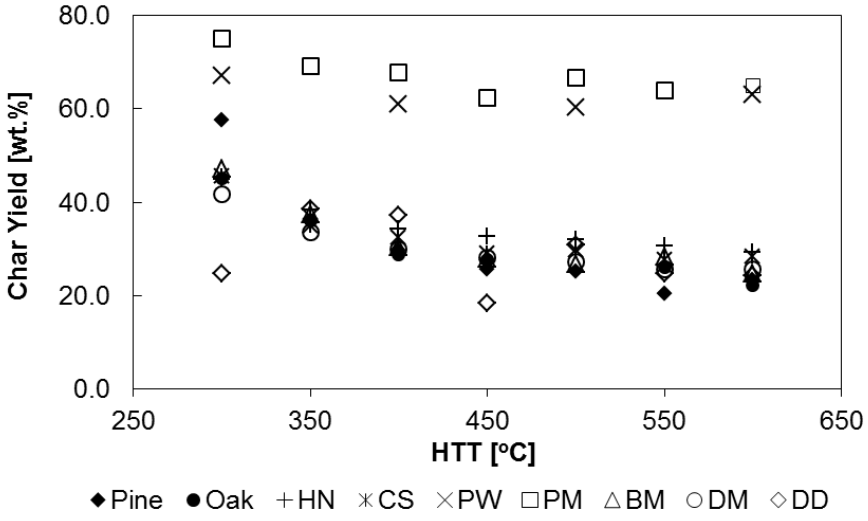

Figure A3-1: Effect of temperature on biochar yield.

In the majority of cases the yield of biochar decreased as temperature was increased due to the release of volatile matter resulting from biomass decomposition as temperature was increased. The highest yields were obtained for PM and PW biochar due to the high ash content of the biochar samples (> 50 %).

A3.3.2 **Direct Oxidation**

The stable-C content (char wt. %) and stable-C yield (feedstock wt. %) were plotted in Figure A3-2 and Figure A3-3 respectively.

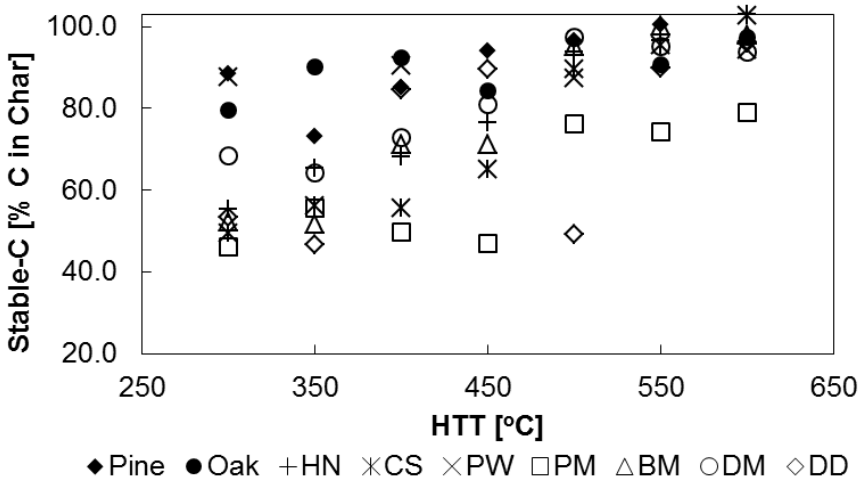

Figure A3-2: Stable-C concentration of Cornell University biochar samples.

As the pyrolysis temperature was increased the percentage of stable-C present within a biochar sample tended to increase as previously shown in Chapter 3, 4 and 5. This is due to the promoted release of volatile matter at elevated temperatures resulting in a higher proportion of biochar C remaining in a stable form. For the majority of Cornell biochar samples this same trend was visible showing an overall significant influence of temperature on stable-C content ($P < 0.0001$). As the production temperature was increased the stable-C content increased to as high as 99 % in some cases. The feedstock choice also seemed to be a determining factor ($P < 0.008$) in the stable-C concentration of biochar shown by woody biomass consistently producing biochar with a higher concentration of stable-C compared to biomass produced from manure/waste material. This could be due to a combination of low C and high ash content commonly found in waste and manure based feedstock influencing the formation of stable structures during pyrolysis. The variation of stable-C content between the different feedstock also appeared to decrease with increasing temperature with the range of values being 78.8 – 100 % at 600^{o}C compared to 46.1 – 87.7 % at 300^{o}C. Although overall the general trend seen in Figure A3-2 was an

increase in stable-C with temperature it is not clear for all samples. Some samples exhibit a drop in stable-C between 400 – 500^{o}C before increasing again at 600^{o}C. This observation could be the result of poor homogeneity of the biochar samples, especially when a small sample mass (1 g) is taken from a large stock of biochar (1 kg) for analysis. The relatively small temperature progression of 50^{o}C and sampling from a large biochar sample could cause variation in results as it is unclear whether the sample analysed is representative of the whole biochar sample. However the homogenous nature of biochar greatly increases at higher pyrolysis temperatures due to the release of volatiles predominantly occurring at lower temperatures. For all samples the stable-C concentration at 600^{o}C was considerably larger than that observed at 300^{o}C for the same biomass.

In addition to studying the relationship between temperature and stable-C the results from direct oxidation of biochar were also compared with stability indicators derived from proximate (fixed C) and ultimate analysis (O:C ratio). A detailed evaluation of the differences between proximate analysis, ultimate analysis and the Edinburgh stability tool for determining biochar stability was given in Chapter 3 and so will not be repeated here. The stable-C content of Cornell biochar samples showed a moderate correlation to the measures of fixed C ($R^2 = 0.541$, $P < 0.0001$) and O:C ratio ($R^2 = -0.609$, $P < 0.0001$). Both fixed C and O:C ratio followed the same trend as stable-C indicating increased biochar stability at elevated temperatures.

The concentration of stable-C is important information however it does not tell the whole story, as char yield decreases with temperature so the overall C sequestration potential would depend on both the stable-C content and yield of biochar. Ideally the stable-C yield would be expressed on a C basis rather than weigh basis so to omit any influence on the char yield from ash concentration. However no information was available for the C concentration of the feedstock used for biochar production therefore the stable-C yield is expressed on a feedstock weight basis and shown in Figure A3-3.

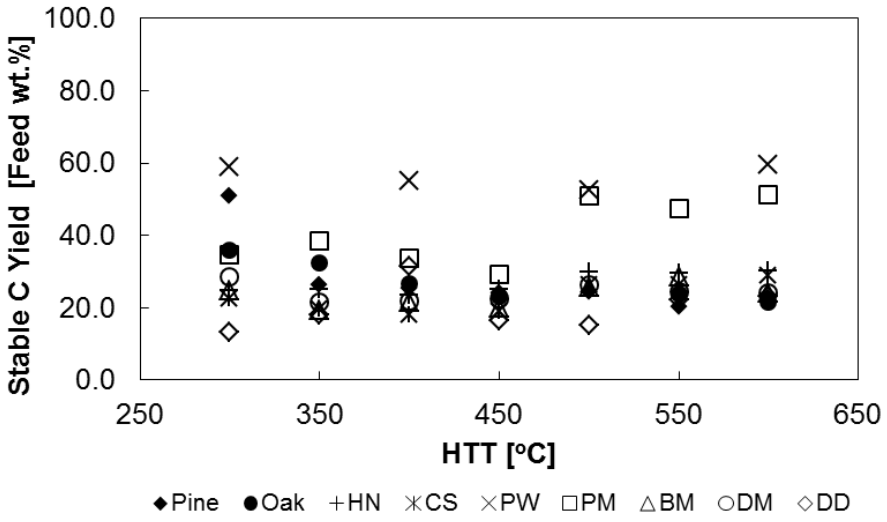

Figure A3-3: Biochar stable-C yield expressed on a feedstock weight basis.

In contrast to the concentration of stable-C, temperature only appeared to have a minor effect on the stable-C yield produced during pyrolysis. In some cases the stable-C yield did increase at elevated temperatures but the majority of samples showed little to no change over the investigated temperature range agreeing with trends observed in Chapter 3. This can demonstrate that although the biochar yield and stable-C content both significantly change with temperature overall the effect may cancel each other out to produce similar yields of stable-C between 300^{o}C and 600^{o}C. This can be extremely important when determining what production conditions to vary when attempting to maximise important physical, chemical and functional biochar properties. However, as previously stated, the stable-C yield is expressed on a feedstock weight basis rather than a C weight basis so the true C sequestration potential cannot be determined.

Not all of the samples analysed were included in the above result section. Some samples were omitted due to one of three reasons: individual samples which were not part of a temperature series; there was a lack of information regarding char yield or pyrolysis temperature used; stability results were greater than 100 % due to unknown reactions potentially related to high ash concentrations. This additional data is presented in Table A3-1.

Table A3-1: Additional stable-C results.

Feedstock	Short Form	Temperature [^{o}C]	Char Yield [wt.%]	C Stability [Char C, wt.%]
Composted Dairy Manure	CDM	500	53.7	79.5
CompDairyManure 1:1 Wood Waste	CDMM	500	43.3	42.2
Raw Dairy Manure	RDM	500	31.3	93.8
STPN3	STPN3-1	220	-	49.1
STPN3	STPN3-2	240	-	43.3
Yard Waste Fall - Leaves	YWFL	500	34.9	102.9
Yard Waste Summer - Grass	YWSG	500	37.3	83.1
Yard Waste Winter - Brush	YWWB	500	26.7	90.9
Musgrave	Musgrave	-	-	108.0
Wood Waste	WW	500	-	78.6
Texas A&M Switchgrass	TSG	-	-	106.3
Texas A&M Chips	TWC	-	-	83.5
West Lorne Bio Oil	WL	-	-	47.4
Kate's Wetland Dynamo	Dynamo	450	-	37.3
Colorado	Colorado	-	-	103.7
Boatang Soybean	BS	500	-	59.4
Boatang Switchgrass	BSG	500	-	17.5

A3.4 **Conclusion**

Cornell University houses a large collection of biochar samples produced under different conditions from a variety of materials. Through analysing this large biochar collection for environmental stability a data set was generated of an equally large size without the time and economic constraints associated with biochar production. This aided in the progression of the PhD project through producing a considerable amount of data on how stable-C content can vary between temperature and feedstock. Furthermore, the results showed a moderate correlation between stable-C and alternative measures of stability (O:C, Fixed C etc.) agreeing with trends seen in Chapter 3; however the correlations were not as strong for the Cornell samples potentially due to the larger variety of biochar analysed.

In addition to benefiting the PhD project the collaboration with Cornell University was designed to improve the accuracy and calibration of the Edinburgh stability tool. This was done by expanding the number of samples which had previously been analysed to include a larger array of biochar samples produced from virgin and non-virgin materials as well as from different types of pyrolysis. This has allowed for trends previously seen while analysing UKBRC biochar to be confirmed through the Cornell analysis while also providing areas of further interest such as the unknown interactions occurring during the analysis of high ash biochar resulting in stable-C measurements of > 100 %. One proposed outcome of the collaboration was the joint investigation into the comparison of the stable-C results with mid-infrared (MIR) spectroscopy data, also measured from the Cornell biochar collection, to attempt to design a statistical model for predicting biochar stability. However any further progress on this study ultimately lies with the availability of those at Cornell to perform the MIR analysis.

A3.5 **Acknowledgments**

Thanks must first go to The Royal Society of Edinburgh and the John Moyes Lessells travel grant, without which the research project would not have been possible. Secondly, I would like to thank Professor Johannes Lehmann for allowing me to join his research group for my time at Cornell University and involving me in the day to day operations of the group. Thanks must go to all the fantastic people I met during my stay in New York State but in particular Dr Akio Enders and Dr Kelly Hanley for their help in settling in at Cornell, hunting down lab equipment and some brilliant memories.

Appendix 4. **Nutrient extraction analysis**

Biochar samples were analysed by the University of Strathclyde to determine the concentration of extractable Ca, K, Mg, Na and P as well as biochar CEC. The following section is therefore a description of the methodology used by the University of Strathclyde for determining the exchangeable bases and CEC.

A4.1 **Nutrient Extraction**

A4.1.1 **Reagents and Standards**

The reagents and standards used during the analysis are listed in Table A4-1.

Table A4-1: List of reagents and standards needed for extractable nutrient analysis.

Chemical	Description
Ammonium acetate	Dissolve 77 g of ammonium acetate in one litre of water
Ethanol	Any high strength (80%+) ethanol solution
Potassium chloride	Dissolve 100 g of KCl in 1000 ml of water. Adjust the pH to 2.5 with 1M HCl (approx. 2.5 ml per litre)
Ammonium stock	Dry and dissolve 0.3821 g NH_4Cl in 1000 ml water for 100 mg L^{-1} stock
Ammonium analysis	• EDTA: 6 g Na_2EDTA/100 ml DI water pH7 • Phenol-nitroprusside :7 g phenol and 34 mg sodium nitroprusside in 100 ml water, store in dark fridge • Buffered hypochlorite: 1.48 g NaOH, 4.98 g Na_2HPO_4, 20 ml 5% NaOCl to 100 ml with water pH11.4-12.2
Chromatography standards	1000 ppm standards of Na, K, Mg,, Ca, Li and Mn bought from a reputable source

A4.1.2 **Leaching Procedure**

A syringe was plugged with glass wool followed by 2 g of sample then again with another plug of glass wool (in triplicate for each sample). An inch of tubing was then attached to each syringe along with a clamp flow regulator. Each syringe was attached to a clamp stand and the tubing was inserted into a 100 ml volumetric flask. The flow regulator was closed and the syringes filled with ammonium acetate. By adjusting the regulator until the flow rate is 2 – 3 drops per second the ammonium acetate was leached in small portions through the column until the volumetric flask was almost full. The flask was then removed, marked and retained for analysis.

The column and tubing was then rinsed with de-ionised water before 50 – 60 ml of ethanol was leached through the sample to remove any excess ammonium not bound to the sample. The tubing was placed in another 100 ml volumetric flask and the leaching procedure repeated with potassium chloride. The leachate was retained for analysis.

A4.1.3 **Exchangeable base analysis by ion chromatography:**

The ammonium acetate leachate (15 ml) was added to a small crucible and heated on a hot plate just below boiling point until all the liquid had evaporated. The dry sample was then ashed at 450˚C for four hours to remove the ammonium acetate. Hydrochloric acid (5 mM, 15 ml) was then added to the cooled crucible and again heated on a hotplate, this time at 70˚C for 20 minutes. The contents of the crucible were poured into a graduated 50 ml centrifuge tube for analysis of Ca, K, Mg and Na using ion chromatograph. The procedure was repeated twice to make the volume up to 50 ml with 5 mM HCl. Ion chromatograph was performed according to the manufacturer's instructions and results expressed in mg kg^{-1}.

A4.1.4 **Total and extractable Phosphorus**

The total concentration of P present within the biochar samples was determined through ashing of the sample at 550^{o}C for 4 hours followed by standard aqua regia digestion (highly corrosive mixture of nitric acid and hydrochloric acid optimally in

a volume ratio of 1:3) with use of a heating block (BS EN 13650, 2001). The remaining residue was then analysed using ICP-OES and expressed in mg kg^{-1}.

The extractable P content of biochar was analysed through application of the standard Olsen method (Olsen *et al.*, 1954; BS7755-3.6, 1995). The approach was originally designed for analyzing soil samples but since adapted for biochar. The analysis is performed by first weighing 1 g of sample into a 50 ml Erlenmeyer flask to which 20 ml of sodium bicarbonate is added and then shaken at $\geq$ 200 rpm for 30 minutes at 24 – 27^{o}C. The extracts were then filtered through a syringe filter and analysed for P by colorimetry or ICP-OES and again expressed in mg kg^{-1}.

A4.1.5 **Ammonium Analysis for CEC determination**

The CEC of biochar was determined through measuring the concentration of ammonium present within the biochar sample (Faithfull, 1985). Ammonium analysis was first conducted by adding 2.5 ml stock to 100 ml matrix to give a working solution of 2.5 mg L^{-1}. Analysis can then be carried out for micro or macro determination. Firstly, micro determination involved adding 60 µL of standard/sample to each microplate. EDTA (15 µL) was then added and allowed to stand for 5 minutes before 25 µL of phenol nitroprusside was added (allowed to stand for a further minute). Following the addition of hypochlorite (50 µL, allowed to stand for 1 minute) and 160 µL of de-ionized water, the microplate was shaken at 37^{o}C for 1 hour. The sample was then allowed to cool for 10 minutes before analysis at 636 nm was performed. Macro determination was carried out by adding 0.5 ml of standard/sample to a centrifuge tube, adding EDTA (0.1ml, stand for 1 minute), phenol nitroprusside (0.2 ml, stand for 1 minute), hypochlorite (0.4 ml, stand for 1 minute), de-ionized water (1.3 ml) and shake for 1 hour at 37^{o}C. Analysis of macro determination was performed at 636 nm using a 1cm path length in a spectrophotometer or by pipetting 300 µL into a microplate. The final CEC of biochar was calculated and expressed as centimoles of charge per kg ($cmol_C$ kg^{-1}).

Appendix 5. **PhD in photographic form**

This PhD has used new experimental design as well as analytical tools for investigating its hypotheses. Therefore the following section is to aid in the understanding of these analytical procedures and experimental schematics through photographic representation of those sections described in Chapter 2.

A5.1 **Systematic sample set**

Figure A5-1: Selection of biochar samples produced by the small-scale batch pyrolysis unit during this PhD.

A5.2 **Pyrolysis set up**

Figure A5-2: Small-scale batch pyrolysis unit including additional components of flow meter, mass spectrometer and gas bag.

Figure A5-3: Photographic representation of the small batch pyrolysis unit schematic presented in Figure 2-1.

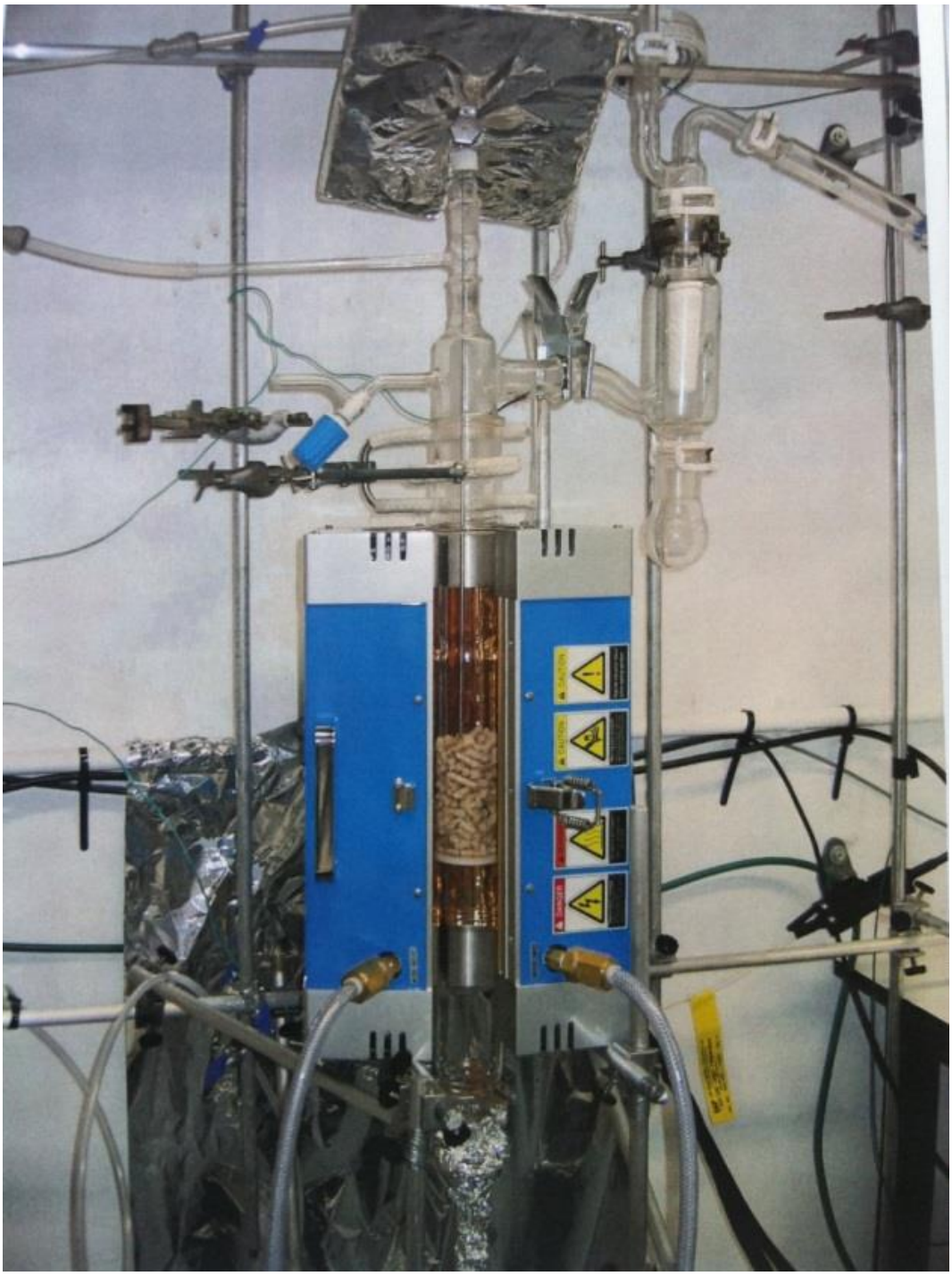

Figure A5-4: Internal positioning of biomass within reactor tube demonstrating the positioning of the feed bed.

A5.3 **Liquid and gas analysis**

Figure A5-5: Quadrupole mass spectrometer used for gas analysis (section 2.4.3.3).

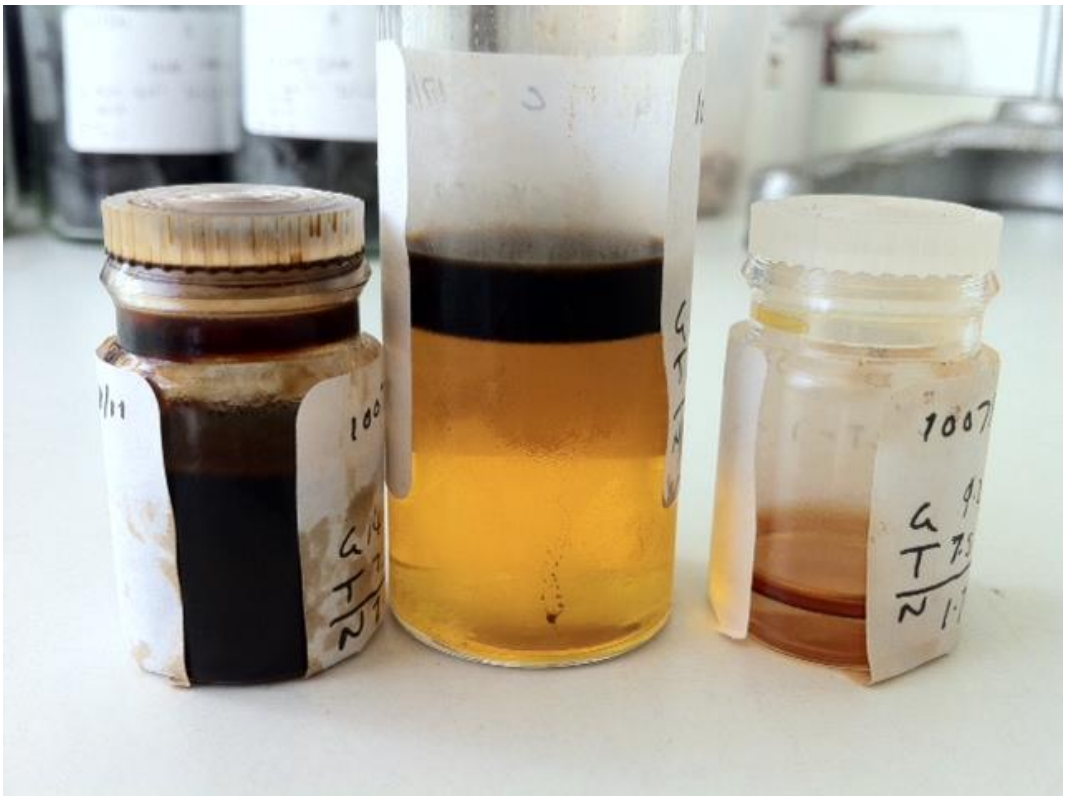

Figure A5-6: Collection of liquid samples in different fractions: Hot trap (left), receiver trap (middle), first cold trap (right) (section 2.3.3).

A5.4 **Biochar functional properties**

A5.4.1 **Stable-C analysis**

Figure A5-7: Samples during chemical and thermal treatment used during the Edinburgh stability tool (section 2.4.2.1.1).

A5.4.2 **Labile-C analysis**

Figure A5-8: Incubation of biochar samples to determine labile-C content (section 2.4.2.1.2).